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Copolymerization of Propylene Oxide with Tetrahydrofuran. IX. The Development of an Empirical Model for the Determination of Kinetic Parameters

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ABSTRACT

The frequently used equation, $-d[M]/dt = k_p [M][P_n*]$, which is applicable to homopolymerization reactions, has been modified to accommodate a copolymerization system involving the comonomers propylene oxide (PO) and tetrahydrofuran (THF). The disappearance of PO (M_1) and THF (M_2) has been related to k_i, k_t, K_{PO}, K_{THF}, r_1, and r_2, and a solution to the ensuing six parameter equation is suggested. This involves calculating r_1 and r_2 with the aid of the Mayo-Lewis equation, $[dM_1/dM_2] = [M_1/M_2][M_1 r_1 +$

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$M_2]/[M_2r_2 + M_1]$, in the form $[dM_1/dM_2] = K[M_1/M_2]^a$ and using the O'Driscoll equations to evaluate r_1 and r_2. The remaining four unknown parameters in the equation are then evaluated, to a first approximation, by optimization techniques such as the Gauss, Gradient, and Monte Carlo methods which in turn are modified by the Monte Carlo simulation method with the aid of an IBM 370/158 computer. A flow diagram describing the steps involved in the computation of rate constants is also included.

INTRODUCTION

The kinetics of cationic propagation reactions in the homopolymerization of cyclic ethers are often represented, in the absence of depolymerization reactions, by Eq. (1) as suggested in the literature [1]:

$$-d[M]/dt = k_p[P_n*][M] \tag{1}$$

In this equation, k_p is the propagation rate constant, $[P_n*]$ is the concentration of propagating species, and [M] is the monomer concentration.

When dealing with copolymerization reactions involving monomers M_1 and M_2, the situation is considerably different. The rates of comonomer disappearance, $-d[M_1]/dt$ and $-d[M_2]/dt$, do not necessarily obey Eq. (1) because the consumption of each of the monomers is related to the concentration of the other and vice versa. Furthermore, the relative reactivities of the monomers play a significant role in determining the nature of the active centers, P_n*. Taking this into consideration, it becomes necessary to modify Eq. (1) to suit it to copolymerization systems involving monomers such as propylene oxide (M_1) and tetrahydrofuran (M_2).

Keeping in mind experimental observations made during various copolymerization studies [2-4], mathematical models have been developed [5] to relate the disappearance of monomers M_1 and M_2 to the different rate constants, viz., k_i $k_{12}[H^+]$, k_t, K_{PO}, K_{THF}, and their respective reactivity ratios, r_1 and r_2. This article deals with the principal results obtained with one of these models.

DEVELOPMENT OF THE MODEL

The Initiation Step

Based on experimental evidence showing that the homopolymerization of THF in a cationic medium generated by boron trifluoride etherate [2], antimony pentachloride [3], or trityl ions [4] takes place only in the presence of PO, it may be assumed that a greater part of the initiation process must involve only PO. One may therefore write

$$PO + H^+ \xrightarrow{k_i} PO^+ \tag{A}$$

The possibility exists that THF^+ may be formed by a scheme similar to that shown in Reaction (A). However, its rate constant must be considered negligible when compared to that of k_i for the formation of PO^+.

The Propagation Steps

In the absence of depropagation, the four propagation reactions of a normal binary copolymerization may be written as

$$PO + PO^+ \xrightarrow{k_{11}} PO^+ \tag{B}$$

$$THF + PO^+ \xrightarrow{k_{12}} THF^+ \tag{C}$$

$$THF + THF^+ \xrightarrow{k_{22}} THF^+ \tag{D}$$

$$PO + THF^+ \xrightarrow{k_{21}} PO^+ \tag{E}$$

However, it has been suggested in the literature [6] that the homopolymerization of THF initiated with $BF_3{:}(C_2H_5)_2O$, $SbCl_5$, or $(C_6H_5)_3C^+PF_6^-$ is reversible in nature. This would mean that Reaction (D), besides having a rate constant k_{22}, must also have a depropagation constant k_{-22}. In the present study it is shown that the depropagation constant k_{-22} is very small when compared to k_{22}. The two constants may be replaced by another, K_{22}, where

$$K_{22} = k_{22}/k_{-22} \tag{2}$$

Making use of the classical thermodynamic relationship,

$$K_{22} = \exp(-\Delta G/RT) \tag{3}$$

and substituting from Ref. 7 values for ΔG_{25} in Eq. (3) (2.2 kcal/mole) and for ΔH_{25} in Eq. (4) (-5.2 kcal/mole), one obtains for K_{22} a value of approximately 40 at 25°C. At lower temperatures (0°C, for example), where many of the experiments have been carried out, the value of K_{22} is still higher (80 or 90) when computed from the expression

$$\partial \ln K_{22}/\partial(1/T) = -\Delta H^{\circ}/R \tag{4}$$

One concludes that the value of k_{-22} must indeed be very small when compared to k_{22} and therefore may be neglected. A similar argument may be used for the case of PO homopolymerization.

The Termination Step

Based on the observation that the polymerization of THF ceases when PO in a reaction mixture has been completely consumed, one is led to assume that the rate-determining step in the termination process must involve an ion dissociation reaction of the type

$$\sim\sim PO^{+} \xrightarrow{k_t} H^{+} + \text{reaction products} \tag{F}$$

The Rate Equations

The rates of comonomer disappearance, based on Reactions (B) to (E), may be written as

$$d[PO]/dt = -k_{11}[PO][PO^{+}] - k_{21}[PO][THF^{+}] \tag{5}$$

$$d[THF]/dt = -k_{12}[THF][PO^{+}] - k_{22}[THF][THF^{+}] \tag{6}$$

$$d[PO^{+}]/dt = k_{i}[PO][H^{+}] - k_{t}[PO^{+}] + k_{21}[PO][THF^{+}] - k_{12}[THF][PO^{+}] \tag{7}$$

$$d[THF^{+}]/dt = k_{12}[THF][PO^{+}] - k_{21}[PO][THF^{+}] \tag{8}$$

The Variations of $[PO^{+}]$ with Time

It has been suggested [8, 9] that, in order to simplify the complex kinetics of polymerization reactions involving four propagation steps

(Eqs. 5 to 8), the assumption of steady-state conditions may be applied where the rate of formation of a monomer active species is equal to its rate of consumption. For example, in the present study, $k_{12}[THF][PO^+]$ may be considered equal to $k_{21}[PO][THF^+]$. Making use of this assumption, Eq. (7) is reduced to

$$d[PO^+]/dt = k_i[PO][H^+] - k_t[PO^+] \tag{9}$$

Rewriting this equation:

$$d[PO^+]/dt + k_t[PO^+] = k_i[PO][H^+] \tag{10}$$

Invoking the well-known Lagrange method for solving differential equations by setting the right-hand side (i.e., $k_i[PO][H^+]$) of Eq. (10) equal to zero, one obtains

$$d[PO^+]/dt + k_t[PO^+] = 0 \tag{11}$$

The solution of Eq. (11) can be written in the form

$$[PO^+] = K\exp(-k_t t) \tag{12}$$

where K is a function of time.

Differentiating Eq. (12) and substituting the results in Eq. (10) yields

$$\frac{dK}{dt}[\exp(-k_t t)] - [Kk_t \exp(-k_t t)] + [Kk_t \exp(-k_t t)] = k_i[PO][H^+] \tag{13}$$

Integrating Eq. (13) between the limits 0 and t yields

$$K = \int_0^t k_i[PO][H^+]\exp(k_t t)\,dt \tag{14}$$

It is difficult to evaluate the integral in Eq. (14) as the variation of PO with time is different in each experiment. During the initial stages of the polymerization, the variation of PO with time may be written, to a first approximation, in the form

$$[\mathrm{PO}] = [\mathrm{PO}]_0 \exp(-K_{\mathrm{PO}} t) \tag{15}$$

where $K_{\mathrm{PO}} = k_{\mathrm{PO}}[P_n^*]$.

Substituting this value for [PO] in Eq. (14) yields

$$K = \int_0^t k_i[\mathrm{H}^+][\mathrm{PO}]_0 \exp(-K_{\mathrm{PO}} t)\exp(k_t t)\, dt \tag{16}$$

On integration, one obtains

$$K = -\frac{k_i[\mathrm{PO}]_0[\mathrm{H}^+]}{K_{\mathrm{PO}} - k_t} \exp(-K_{\mathrm{PO}} t + k_t t) + C \tag{17}$$

Combining Eqs. (12) and (17) yields

$$[\mathrm{PO}^+] = \left[C - \frac{k_i[\mathrm{PO}]_0[\mathrm{H}^+]}{K_{\mathrm{PO}} - k_t} \exp(-K_{\mathrm{PO}} t + k_t t)\right]\exp(-k_t t) \tag{18}$$

In the limit t = 0, $[\mathrm{PO}^+] = 0$ and $C = k_i[\mathrm{PO}]_0[\mathrm{H}^+]/(K_{\mathrm{PO}} - k_t)$. Therefore,

$$[\mathrm{PO}^+] = \frac{k_i[\mathrm{PO}]_0[\mathrm{H}^+]}{K_{\mathrm{PO}} - k_t}\left[\exp(-k_t t) - \exp(-K_{\mathrm{PO}} t)\right] \tag{19}$$

The Variations of [THF] with Time

The assumption of steady-state conditions in Eq. (12) yields

$$[\mathrm{THF}^+] = k_{12}[\mathrm{THF}][\mathrm{PO}^+]/k_{21}[\mathrm{PO}] \tag{20}$$

Combining Eqs. (6) and (20), one obtains

$$\frac{d[\mathrm{THF}]}{dt} = -k_{12}[\mathrm{PO}^+][\mathrm{THF}] - k_{22}[\mathrm{THF}]\left[\frac{k_{12}[\mathrm{PO}^+][\mathrm{THF}]}{k_{21}[\mathrm{PO}]}\right] \tag{21}$$

or

$$\frac{d[\mathrm{THF}]}{dt} = -k_{12}[\mathrm{PO}^+][\mathrm{THF}]\left[1 + \frac{k_{22}}{k_{21}}\frac{[\mathrm{THF}]}{[\mathrm{PO}]}\right] \tag{22}$$

or yet again

$$\frac{d[\mathrm{THF}]}{dt} = -k_{12}[\mathrm{PO}^+][\mathrm{THF}]\left[1 + r_2\frac{[\mathrm{THF}]}{[\mathrm{PO}]}\right] \tag{23}$$

Using the expression for $[\mathrm{PO}^+]$ from Eq. (19) in Eq. (23), one obtains

$$\frac{d[\mathrm{THF}]}{dt} = -k_{12}\frac{k_i[\mathrm{PO}]_0[\mathrm{H}^+]}{K_{\mathrm{PO}} - k_t}\left[\exp(-k_t t) - \exp(-K_{\mathrm{PO}}t)\right][\mathrm{THF}]\left[1 + r_2\frac{[\mathrm{THF}]}{[\mathrm{PO}]}\right] \tag{24}$$

Substituting A for the expression $k_i[\mathrm{PO}]_0[\mathrm{H}^+]/(K_{\mathrm{PO}} - k_t)$ and rearranging terms, Eq. (24) reduces to

$$\frac{d[\mathrm{THF}]}{[\mathrm{THF}]} = -k_{12}A\left[\exp(-k_t t) - \exp(-K_{\mathrm{PO}}t)\right]\left[1 + r_2\frac{[\mathrm{THF}]}{[\mathrm{PO}]}\right]dt \tag{25}$$

Integrating Eq. (25) between the limits 0 and t leads to

$$[\mathrm{THF}] = [\mathrm{THF}]_0 \exp\left(-k_{12} A \int_0^t \left[\exp(-k_t t) - \exp(-K_{PO} t)\right] \left[1 + r_2 \frac{[\mathrm{THF}]}{[\mathrm{PO}]}\right] dt\right) \tag{26}$$

Under corresponding conditions, one can write a similar expression for [PO]:

$$[\mathrm{PO}] = [\mathrm{PO}]_0 \exp\left(-k_{12} A \int_0^t \left[\exp(-k_t t) - \exp(-K_{PO} t)\right] \left[r_1 + \frac{[\mathrm{THF}]}{[\mathrm{PO}]}\right] dt\right) \tag{27}$$

In order to evaluate the integrals in Eqs. 26 and 27, one must know in what manner the ratio [THF]/[PO] varies with time.

The Variations of [THF]/[PO] with Time

The disappearance of THF with time in the initial stages of the reaction may be considered to obey a law similar to that followed by PO (Eq. 15). Thus

$$[\mathrm{THF}] = [\mathrm{THF}]_0 \exp(-K_{THF} t) \tag{28}$$

where $K_{THF} = k_{THF}[P_n^*]$.

From Eqs. (15) and (28), one can write that

$$\frac{[\mathrm{THF}]}{[\mathrm{PO}]} = \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{\exp(-K_{THF} t)}{\exp(-K_{PO} t)} \tag{29}$$

Substituting this expression for [THF]/[PO] in Eq. (26), one obtains

$$[\mathrm{THF}] = [\mathrm{THF}]_0 \exp\left(-k_{12} A \int_0^t \left[\exp(-k_t t) - \exp(-K_{PO} t)\right] \left[1 + r_2 \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{\exp(-K_{THF} t)}{\exp(-K_{PO} t)}\right] dt\right) \tag{30}$$

Integration of Eq. (30) now yields

$$\begin{aligned}
[\mathrm{THF}] = [\mathrm{THF}]_0 \exp\Bigg(-k_{12} A \Bigg[& \frac{1}{k_t}(1 - \exp(-k_t t)) - \frac{1}{K_{PO}}(1 - \exp(-K_{PO} t)) \\
& + r_2 \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{1 - \exp(-K_{THF} t - k_t t + K_{PO} t)}{K_{THF} + k_t - K_{PO}} \\
& - r_2 \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{1 - \exp(-K_{THF} t)}{K_{THF}} \Bigg]\Bigg) \qquad (31)
\end{aligned}$$

and for PO a corresponding equation:

$$\begin{aligned}
[\mathrm{PO}] = [\mathrm{PO}]_0 \exp\Bigg(-k_{12} A \Bigg[& \frac{r_1}{k_t}(1 - \exp(-k_t t)) - \frac{r_1}{K_{PO}}(1 - \exp(-K_{PO} t)) \\
& + \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{1 - \exp(-K_{THF} t - k_t t + K_{PO} t)}{K_{THF} + k_t - K_{PO}} \\
& - \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{1 - \exp(-K_{THF} t)}{K_{THF}} \Bigg]\Bigg) \qquad (32)
\end{aligned}$$

The validity of Eqs. (31) and (32) may be tested by calculating the values of [THF] and [PO] at zero time where one should obtain $[\mathrm{THF}] = [\mathrm{THF}]_0$ and $[\mathrm{PO}] = [\mathrm{PO}]_0$. For large values of t, Eqs. (31) and (32) can be reduced to

$$\begin{aligned}
[\mathrm{THF}] = [\mathrm{THF}]_0 \exp\Bigg(-k_{12} A \Bigg[& \frac{1}{k_t} - \frac{1}{K_{PO}} + \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{r_2}{K_{THF} + k_t - K_{PO}} \\
& - \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{r_2}{K_{THF}} \Bigg]\Bigg) \qquad (33)
\end{aligned}$$

and

$$[PO] = [PO]_0 \exp\left(-k_{12}A\left[\frac{r_1}{k_t} - \frac{r_1}{K_{PO}} + \frac{[THF]_0}{[PO]_0}\,\frac{1}{K_{THF} + k_t - K_{PO}} - \frac{[THF]_0}{[PO]_0}\,\frac{1}{K_{THF}}\right]\right) \tag{34}$$

Thus, if one knows the manner in which THF and PO disappear with time, one can solve these equations for the different rate constants with the help of optimization processes [10-16]; however, in order to get more reliable values, one must study the disappearance of the comonomers with five or six different comonomer proportions which is useful also for the computation of r_1 and r_2. This reduces Eqs. (33) and (34) to four unknown parameters instead of six.

The Evaluation of Reactivity Ratios

The reactivity ratios of comonomers can be calculated by the well-known Mayo-Lewis [17] equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\,\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \tag{35}$$

Recently [18, 19], this equation has been transformed to the form

$$\frac{d[M_1]}{d[M_2]} = K\left[\frac{[M_1]}{[M_2]}\right]^a \tag{36}$$

where K and a are constants. O'Driscoll and co-workers [20] have shown that, with any two comonomer feed compositions, x_1 and x_2, where $x_1 = [M_1]_1/[M_2]_1$, and $x_2 = [M_1]_2/[M_2]_2$, the values of r_1 and r_2 may be evaluated from the expressions

$$r_1 = -\frac{Kx_1^{(a-2)}x_2^{(a-2)}(x_1 - x_2)}{x_1^{(a-2)} - x_2^{(a-2)}} - \frac{x_1^{(a-1)} - x_2^{(a-1)}}{x_1x_2(x_1^{(a-2)} - x_2^{(a-2)})} \tag{37}$$

$$r_2 = -\frac{x_1^{(a-1)} - x_2^{(a-1)}}{x_1^{(a-2)} - x_2^{(a-2)}} - \frac{x_1 - x_2}{Kx_1x_2\left(x_1^{(a-2)} - x_2^{(a-2)}\right)} \tag{38}$$

The power constant a can be evaluated from a log-log plot of $d[M_1]/d[M_2]$ as a function of the ratio $[M_1]/[M_2]$; K is obtained by setting $[M_1]/[M_2]$ equal to 1 in Eq. (35). Thus

$$K = (r_1 + 1)/(r_2 + 1) \tag{39}$$

The Calculation of the Rate Constants k_{12} and k_{11}

When one computes the rate constants from Eqs. (33) and (34) with the help of optimization processes, individual values of k_t, K_{PO}, and K_{THF} are easily obtained. The constants k_i and k_{12}, however, are obtained only in the form $k_ik_{12}[H^+]$ and it is difficult to separate them without having to make further assumptions. Nevertheless, an attempt has been made to calculate the value of k_{12} separately on the assumption that if the initiation process is rapid and all of the H^+ has been consumed before the comonomers have begun to disappear, then the expression $k_i[PO][H^+]$ in Eq. (7) is rendered negligible. Equation (7) may then be written in a more concise form as

$$d[PO^+]/dt = -k_t[PO^+] + k_{21}[PO][THF^+] - k_{12}[THF][PO^+] \tag{40}$$

Invoking steady-state conditions, one obtains

$$d[PO^+]/dt + k_t[PO^+] = 0 \tag{41}$$

Saegusa [1] used a similar expression, viz., $d[P_n^*]/dt + k_t[P_n^*] = 0$, for the evaluation of k_t in the homopolymerization of THF. The concentrations of active centers, P_n^*, were determined at different intervals by the phenoxyl end-capping method to compute $d[P_n^*]/dt$. Log-log plots of $d[P_n^*]/dt$ vs $[P_n^*]$ yielded a straight line from which k_t was evaluated.

In the present study the concentrations of active centers are not known and an alternate approach has had to be developed in order to resolve the problem. The solution of Eq. (41) may again be written in an exponential form:

$$[PO^+] = K \exp(-k_t t) \tag{42}$$

At zero time, $K = [PO^+]_0$. Based on the earlier observation of fast initiation, one can assume that at time $t \approx 0$, $[PO^+]_0 \equiv [H^+]_0$. Thus

$$[PO^+] = [H^+]_0 \exp(-k_t t) \tag{43}$$

Combining Eqs. (43), (5), and (6) and making use of steady-state conditions where $k_{12}[THF][PO^+] = k_{21}[PO][THF^+]$, one may write Eqs. (5) and (6) to read

$$\frac{d[PO]}{dt} = -k_{11}[PO][H^+]_0 \exp(-k_t t) - k_{12}[THF][H^+]_0 \exp(-k_t t) \tag{44}$$

and

$$\frac{d[THF]}{dt} = -k_{12}[THF][H^+]_0 \exp(-k_t t) - k_{22}[THF]$$

$$\frac{k_{12}[THF]}{k_{21}[PO]} [H^+]_0 \exp(-k_t t) \tag{45}$$

The solution of Eqs. (44) and (45) take on the forms

$$[PO] = [PO]_0 \exp\left(-k_{12}[H^+]_0 \int_0^t \exp(-k_t t)\right.$$

$$\left.\left[r_1 + \frac{[THF]_0}{[PO]_0} \frac{\exp(-K_{THF} t)}{\exp(-K_{PO} t)}\right] dt\right) \tag{46}$$

$$[\mathrm{THF}] = [\mathrm{THF}]_0 \exp\left(-k_{12}[\mathrm{H}^+]_0 \int_0^t \exp(-k_t t) \left[1 + r_2 \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{\exp(-K_{\mathrm{THF}} t)}{\exp(-K_{\mathrm{PO}} t)}\right] dt\right) \tag{47}$$

Integrating Eqs. (46) and (47) between the limits 0 and t yields

$$[\mathrm{PO}] = [\mathrm{PO}]_0 \exp\left(-k_{12}[\mathrm{H}^+]_0 \left[\frac{r_1}{k_t}(1 - \exp(-k_t t)) + \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{1 - \exp(-K_{\mathrm{THF}} t - k_t t + K_{\mathrm{PO}} t)}{k_t + K_{\mathrm{THF}} - K_{\mathrm{PO}}}\right]\right) \tag{48}$$

$$[\mathrm{THF}] = [\mathrm{THF}]_0 \exp\left(-k_{12}[\mathrm{H}^+]_0 \left[\frac{1}{k_t}(1 - \exp(-k_t t)) + r_2 \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{(1 - \exp(-K_{\mathrm{THF}} t - k_t t + K_{\mathrm{PO}} t)}{k_t + K_{\mathrm{THF}} - K_{\mathrm{PO}}}\right]\right) \tag{49}$$

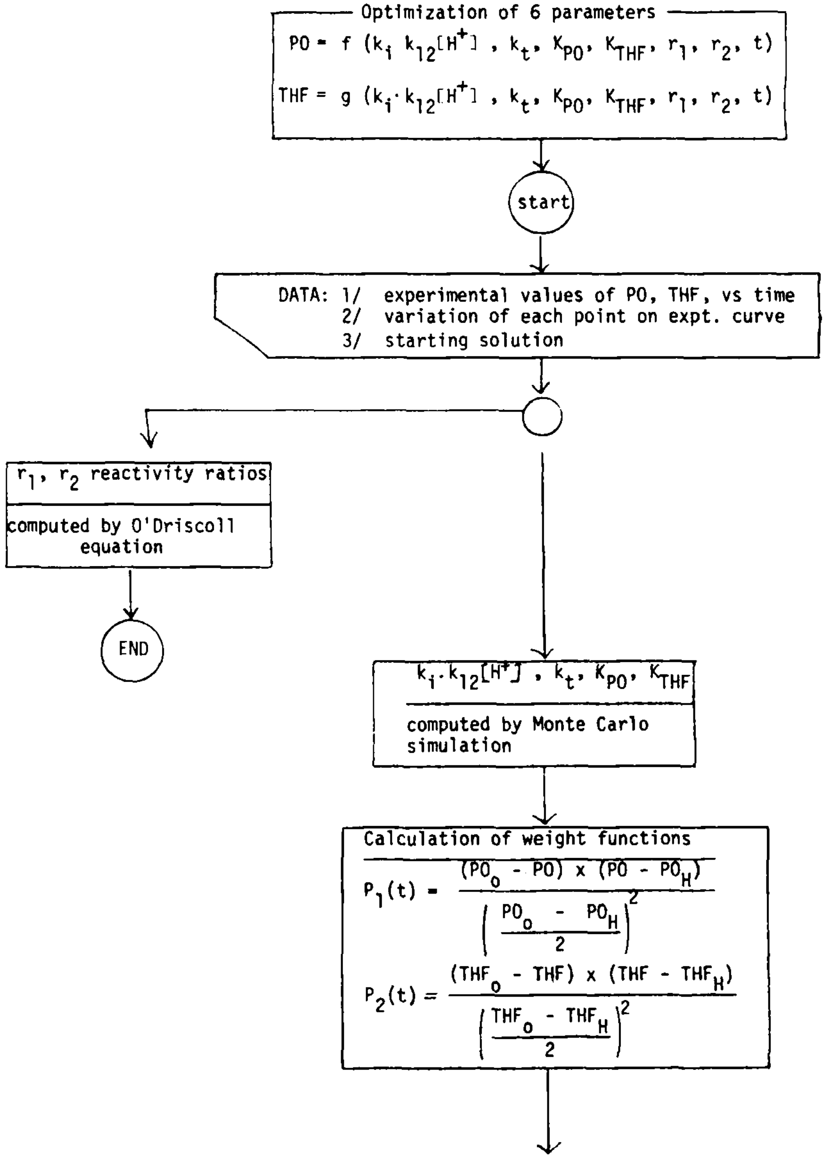
and for high values of t:

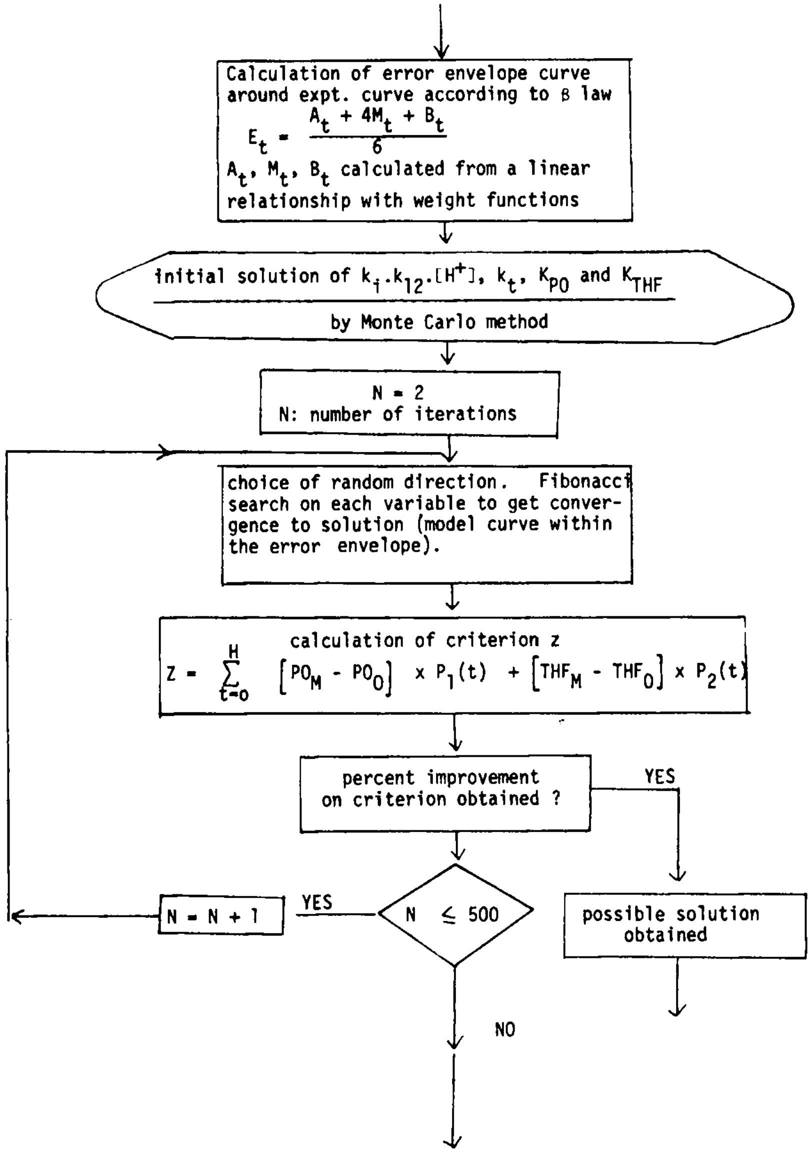
$$[\mathrm{PO}] = [\mathrm{PO}]_0 \exp\left(-k_{12}[\mathrm{H}^+]_0 \left[\frac{r_1}{k_t} - \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{1}{K_{\mathrm{PO}} - k_t - K_{\mathrm{THF}}}\right]\right) \tag{50}$$

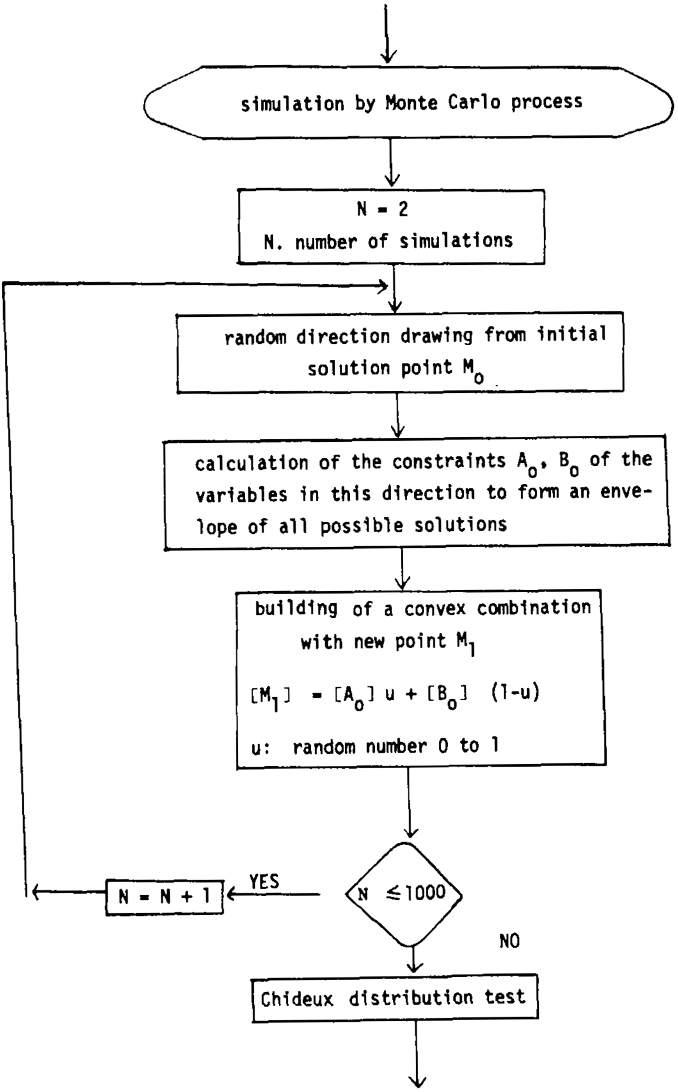
and

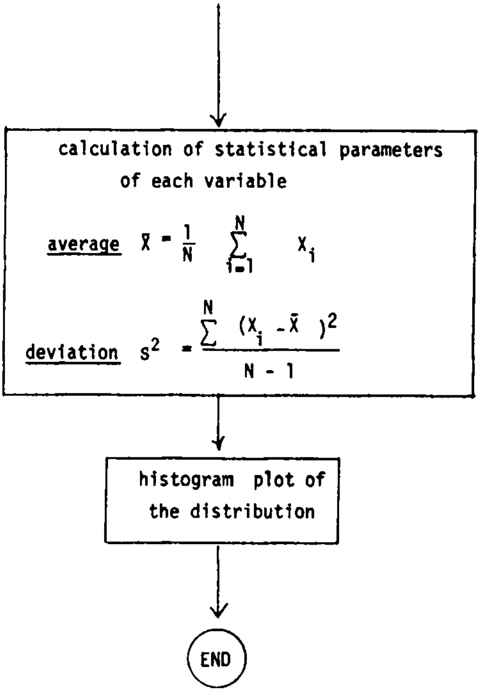
$$[\mathrm{THF}] = [\mathrm{THF}]_0 \exp\left(-k_{12}[\mathrm{H}^+]_0 \left[\frac{1}{k_t} - r_2 \frac{[\mathrm{THF}]_0}{[\mathrm{PO}]_0} \frac{1}{K_{\mathrm{PO}} - k_t - K_{\mathrm{THF}}}\right]\right) \tag{51}$$

FLOW DIAGRAM




Calculation of error envelope curve around expt. curve according to β law
$E_t = \frac{A_t + 4M_t + B_t}{6}$
A_t, M_t, B_t calculated from a linear relationship with weight functions
initial solution of $k_i.k_{12}.[H^+]$, k_t, K_{PO} and K_{THF}
by Monte Carlo method
N = 2
N: number of iterations
choice of random direction. Fibonacci search on each variable to get convergence to solution (model curve within the error envelope).
calculation of criterion z
$Z = \sum_{t=o}^{H} \left[PO_M - PO_O\right] \times P_1(t) + \left[THF_M - THF_O\right] \times P_2(t)$
percent improvement on criterion obtained ?
YES
possible solution obtained
N ≤ 500
YES
N = N + 1
NO


simulation by Monte Carlo process
N = 2
N. number of simulations
random direction drawing from initial solution point M_0
calculation of the constraints A_0, B_0 of the variables in this direction to form an envelope of all possible solutions
building of a convex combination with new point M_1
$[M_1] = [A_0]\,u + [B_0]\,(1-u)$
u: random number 0 to 1
$N \leq 1000$
YES
N = N + 1
NO
Chideux distribution test



Making use of Eqs. (48) and (49), one can calculate accurately the values of $k_{12}[H^+]$. With the knowledge of r_1, the value of k_{11} is also easily computed. Furthermore, if one compares the value of $k_i k_{12}[H^+]$ with that of $k_{12}[H^+]_0$, one can get an idea about the individual value of k_i. For precise values of k_i, one needs to know the exact value of $[H^+]$ for which the phenoxyl end-capping method of Saegusa [1] may be used. One may also make a plot of $k_i[H^+]$ as a function of different initial concentrations of the catalyst, i.e., $[H^+]_0$, in order to determine k_i.

Computing Values of the Kinetic Constants

The procedure discussed below for the calculation of kinetic constants may be used only after having calculated the reactivity ratios separately. Initially, Gauss and Gradient optimization can be used to separate the four unknown constants; however, because of inherent problems in these methods, it is sometimes difficult to obtain optimum points because of the slow convergence toward these points. Furthermore, the optimization process may stop at a local optimum point and thus yield values which have no real significance.

In order to overcome these difficulties, the Monte Carlo simulation method, in which random processes and statistical concepts have some meaning, may be tried. This method is based on Fibonacci search in one randomly determined direction and leads to an optimum solution which is defined here as the point which satisfies the minimum criterion (Z) described by

$$Z = \sum_{t=0}^{H} F[S_0(t) - S_M(t)]P(t) \tag{52}$$

where H is the duration of the reaction, S_0 (t) is the experimental value at time t, and $S_M(t)$ is the value calculated from a model at time t and P(t), the weight function describing the deviation between the model and the experimental value.

The simulation process suggested here for the computations involves three principal steps:

1. Finding a basic initial solution with either the gradient or the Monte Carlo methods.
2. Building up of a simulation process around this solution by Fibonacci search and creating an envelope which carries all the possible combinations between the variables. This has been defined in the flow diagram as the constraints of each variable.
3. Performing the statistical compilation for each of the parameters.

See the flow diagram on pages 1232-1235.

Example of Computations Leading to the Evaluation of Rate Constants

Earlier [2], the copolymerization of PO with THF was reported to have been initiated with $BF_3:(C_2H_5)_2O$ in the presence of 1,2-propanediol as cocatalyst and dichloroethane as solvent. Data—comonomer concentrations vs time—for experiment No. 65-19 in Ref. 2b is given in Table 1. Based on further data representing the variation of rates of comonomer disappearance as a function of comonomer concentrations, drawn from Ref. 2a, the reactivity ratios

TABLE 1. A Comparison of Experimental and Calculated Values for Variations of Comonomer Concentrations with Time, Obtained on Using the Best Initial Solution (Expt. no. 65-19)[2]

Time (min)	$[PO]_{Expt}$ (mole/liter)	$[PO]_{Model}$ (mole/liter)	[PO] deviation	$[THF]_{Expt}$ (mole/liter)	$[THF]_{Model}$ (mole/liter)	[THF] deviation
0	3.40	3.40	0.00	3.35	3.35	0.00
25	2.95	3.15	-0.20	2.95	3.15	-0.20
50	2.50	2.63	-0.13	2.60	2.70	-0.10
75	2.08	2.08	0.00	2.25	2.20	0.05
100	1.62	1.62	0.00	1.90	1.76	0.14
125	1.22	1.25	-0.03	1.55	1.39	0.16
150	0.93	0.98	-0.05	1.25	1.10	0.15
175	0.65	0.79	-0.14	1.00	0.89	0.11

r_1 and r_2 calculated with the O'Driscoll [20] equations (42 to 44 in the present text) for this particular experiment, were found to have values of 0.46 and 0.45, respectively. Rate constants K_{PO} and K_{THF} were computed from the initial slopes of plots of comonomer concentrations vs time. Their respective values were found to be 5.9×10^{-3}/min and 7.0×10^{-3}/min. The other two unknown constants, viz., $k_i k_{12}$ $[H^+]$liter/mole-min^2 and k_t/min were assumed to have values ranging between $(1 \text{ and } 10) \times 10^{-3}$/min for the former and $(10 \text{ and } 20) \times 10^{-3}$/min for the latter in order to start the program. These two values were taken from the work of Saegusa [1] on the polymerization of cyclic ethers in general. The Monte Carlo method was now applied and after some 400 iterations the best initial solution gave the following: $k_i k_{12}$ $[H^+] = 4.0 \times 10^{-3}$ liter/mole-min^2; $k_t = 14.0 \times 10^{-3}$/min; $K_{PO} = 5.9 \times 10^{-3}$/min; $K_{THF} = 7.0 \times 10^{-3}$/min; $r_1 = 0.46$ and $r_2 = 0.45$.

These values were substituted into the mathematical model and data on the comonomer concentrations vs time was obtained. This data is compared with the experimental values listed in Table 1. From this table it is apparent that, with some modification of the initial solution, one should obtain an envelope for the final solution. Monte Carlo simulation method was now applied and after some 1000 simulations the statistical compilation for each of the constants was obtained in the form of distributions shown in Table 2 to 5, out of which a unique mean average value was obtained for each of the four unknown constants. The results, as read from Tables 2 to 5, are as follows: $k_i k_{12}[H^+] = 6.46 \times 10^{-5}$ liter/mole-min^2, $k_t = 16.86 \times 10^{-3}$/min, $K_{PO} = 7.25 \times 10^{-3}$/min, and $K_{THF} = 4.99 \times 10^{-3}$/min. The values of K_{PO} and K_{THF} may further be reduced to k_{PO} and k_{THF} by dividing these by the number of active centers. Similarly, the value of k_i may be obtained by substituting the values of k_{12} (as calculated from Eqs. 45 to 56 of the present text) and $[H^+]$ determined by the phenoxyl end-capping method of Saegusa [1]. This model is presently being tested on the major portion of the experimental work carried out in this laboratory on the copolymerization of PO with THF. The results will be reported in the near future.

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TABLE 2. Statistical Weight Distribution of the Constant $k_i k_{12}[H^+]$

True variable $\times 10^5$ (liter/mole-min^2)	Reduced variable	Statistical weight distribution	%
		0 5 10 15 20	
4.70	-2.25	*	0.5
4.89	-2.00	**	1.0
5.09	-1.75	**	1.0
5.28	-1.50	*****	2.5
5.48	-1.25	********	4.0
5.68	-1.00	**************	7.0
5.87	-0.75	****************	8.0
6.07	-0.50	******************	9.0
6.27	-0.25	***********************	11.5
6.46	-0.00	*********************	10.5
6.66	0.25	**********************	11.0
6.86	0.50	******************	9.0
7.05	0.75	************	6.0
7.25	1.00	************	6.0
7.44	1.25	******	3.0
7.64	1.50	******	3.0
7.84	1.75	****	2.0
8.03	2.00	**	1.0
8.23	2.25	****	2.0
8.43	2.50	**	1.0

TABLE 3. Statistical Weight Distribution of the Constant k_t

True variable $\times 10^3$ (min^{-1})	Reduced variable	Statistical weight distribution 0 5 10 15 20	%
12.81	-1.75	**	1.0
13.40	-1.50	*	0.5
13.97	-1.25	******	3.0
14.55	-1.00	*************	6.5
15.13	-0.75	**************	7.0
15.70	-0.50	***********************************	17.5
16.28	-0.25	*************************	12.5
16.86	0.00	*********************	10.5
17.44	0.25	*******************	9.5
18.02	0.50	**********	5.0
18.60	0.75	*******	3.5
19.17	1.00	************	6.0
19.75	1.25	***********	5.5
20.33	1.50	**	1.0
20.90	1.75	*********	4.5
21.48	2.00	*******	3.5

TABLE 4. Statistical Weight Distribution of the Constant K_{PO}

True variable $\times 10^3$ (min^{-1})	Reduced variable	Statistical weight distribution	%
		0 5 10 15 20	
0.83	-3.00	*****	2.5
1.36	-2.75	****	2.0
1.90	-2.50	**	1.0
2.43	-2.25	***	1.5
2.97	-2.00	***	1.5
3.50	-1.75	**	1.0
4.04	-1.50	**	1.0
4.57	-1.25	****	2.0
5.11	-1.00	*****	2.5
5.64	-0.75	****	2.0
6.18	-0.50	**************	7.0
6.71	-0.25	*************	6.5
7.25	-0.00	**************************	13.0
7.78	0.25	********************************	16.0
8.32	0.50	*********************************	16.5
8.85	0.75	********************	10.0
9.40	1.00	*****************	8.5
9.92	1.25	*********	4.5
10.46	1.50	*	0.5

TABLE 5. Statistical Weight Distribution of the Constant K_{THF}

True variable × 10^3 (min^{-1})	Reduced variable	Statistical weight distribution	%
		0 5 10 15 20	
0.22	-2.25	*******************	9.5
0.75	-2.00	****	2.0
1.28	-1.75		0.0
1.80	-1.50	*	0.5
2.33	-1.25	*****	2.5
2.86	-1.00	**	1.0
3.40	-0.75	*******	3.5
3.92	-0.50	**************	7.0
4.45	-0.25	*****************	8.5
5.00	-0.00	*************************	12.5
5.51	0.25	*****************************	14.5
6.04	0.50	*****************************	14.5
6.57	0.75	************************	12.0
7.10	1.00	*******	3.5
7.63	1.25	******	3.0
8.16	1.50	***********	5.5
8.70	1.75	**	1.0
9.22	2.00		0.0

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REFERENCES

[1] T. Saegusa, in Polymerization of Heterocyclics (O. Vogl and J. Furukawa, eds.), Dekker, New York, 1973, pp. 5-34.
T. Saegusa and S. Matsumoto, J. Polym. Sci., A-1, 6, 1559 (1968); Macromolecules, 1, 442 (1968).

[2] (a) L. P. Blanchard, J. Singh, and M. D. Baijal, Can. J. Chem., 44, 2679 (1966). (b) M. D. Baijal and L. P. Blanchard, J. Polym. Sci., 23, 157 (1968).

[3] E. J. Alvarez, V. Hornof, and L. P. Blanchard, J. Polym. Sci., Polym. Chem. Ed., 10, 1895 (1972).

[4] L. P. Blanchard, G. G. Gabra, and S. L. Malhotra, Ibid., 13, 1619 (1975).

[5] C. Raufast, Thèse de Maitrise, Université Laval, 1969.

[6] P. Dreyfuss and M. P. Dreyfuss, Advan. Polym. Sci., 4, 528 (1967).

[7] M. Tetsuro, Bull. Chem. Soc., Japan, 39(1), 25 (1966).

[8] C. E. H. Bawn, The Chemistry of High Polymers, Butterworths, London, 1948, p. 88.

[9] R. B. Cundall, in The Chemistry of Cationic Polymerizations (P. H. Plesch, ed.), Pergamon, New York, 1963, p. 552.

[10] A. Kaufman and G. Desbazeilles, La méthode du chemin critique, Dunod, Paris, 1965.

[11] D. Wilde, Optimum Seeking Method, Prentice-Hall, Englewood Cliffs, New Jersey, 1964.

[12] L. Lapidus, Chem. Eng. Prog. Symp. Ser. 36, 126 (1961).

[13] L. Cooper and D. Steinberg, Introduction to Methods of Optimization, Saunders, Philadelphia, 1970.

[14] J. M. Hammersley, Les méthodes de Monte Carlo, Dunod, Paris, 1965.

[15] L. S. Lasdon, Optimization Theory for Large Systems, Macmillan, New York, 1970.

[16] P. L. Hennequin, Méthodes de Monte Carlo et techniques de simulation, Presses de l'Université Laval, Québec, Canada, 1967.

[17] F. R. Mayo and F. M. Lewis, J. Amer. Chem. Soc., 66, 1594 (1944).

[18] K. F. O'Driscoll, J. Polym. Sci., 57, 721 (1962).
[19] V. Jaacks, Makromol. Chem., 105, 289 (1967).
[20] T. Higashimura, T. Masuda, and K. F. O'Driscoll, J. Polym. Sci., B, 6, 841 (1968).

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