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AN APPROXIMATE KINETIC TREATMENT OF SLOW-INITIATED LIVING POLYMERIZATION. I. FIRST-ORDER INITIATION AND PROPAGATION

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ABSTRACT

A new method for deriving the initiation rate constant for a slow-initiated living polymerization process in which all reactions are first order with respect to all participants is presented. The method is based upon an approximate analytical solution of the set of differential equations modeling this class of processes. The solution is found by asymptotic expansion of the unknown functions, using a dimensionless parameter which characterizes the process.

INTRODUCTION

The kinetics of slow-initiated living polymerization have been investigated quite extensively [1-10], one of the main problems being that of determining the reaction rate constants. This problem does not have a simple solution, not even in the simple case of a polymerization process in which both initiation and propagation are first order with respect to all participants (the methods already in use do not always predict the reaction rate constants with a satisfactory precision [14]). An accurate determination of the reaction rate constants would require knowledge of an exact analytical solution of the set of differential equations modeling the process. Since such a solution cannot be found [9], we have derived an approximate analytical solution of this set which allows us to calculate the reaction rate constants.

THEORY

The process of a slow-initiated living polymerization in which both initiation and propagation are first order with respect to monomer concentration and catalyst and active center concentrations, respectively, is described by

$$I + M \longrightarrow P^*, \quad \text{initiation;}$$

$$P^* + M \longrightarrow \text{polymer}, \quad \text{propagation;}$$

where I stands for initiator (or catalyst), M is the monomer, and P* is an active center. The corresponding set of differential equations is

$$\begin{aligned} d[I]/dt &= -k_i[M][I], \\ d[M]/dt &= -k_p[P][M] - k_i[I][M]. \end{aligned} \qquad (1)$$

The initial conditions are $[I]|_{t=0} = [I]_0$, $[M]|_{t=0} = [M]_0$; and from a simple catalyst balance: $[P^*] = [I]_0 - [I]$.

The assumption of a slow-initiated polymerization is described by the $k_i << k_p$ inequality, which enables us to neglect the term $k_i[I][M]$ in the second equation of Set (1), which becomes

$$\begin{aligned} d[P^*]/dt &= k_i([I]_0 - [P^*])[M], \\ d[M]/dt &= -k_p[P^*][M], \end{aligned} \qquad (2)$$

with $[M]|_{t=0} = [M]_0$ and $[P^*]|_{t=0} = 0$.

Let us define the following dimensionless parameters: $m = [M]/[M]_0$, $p = [P^*]/[I]_0$, $\tau = k_i[M]_0 t$.

In fast-initiated polymerizations in which propagation is first-order with respect to monomer concentration, plots of $\ln([M]/[M]_0)$ against time yield straight lines. It is thus useful to substitute $q = -\ln m$. We shall further make use of the dimensionless parameter $\epsilon = k_p[I]_0/(k_i[M]_0)$, first suggested by Pepper [8]. With these transformations, the set of Eq. (2) may be written

$$dp/d\tau = (1 - p) \exp(-q),$$
$$dq/d\tau = \epsilon p. \tag{3}$$

If $\epsilon < 1$, the method of regular perturbations [11] is applicable. In order to do this, p and q are expanded in a power series of ϵ:

$$p(\tau,\epsilon) = p_0(\tau) + \epsilon p_1(\tau) + \epsilon^2 p_2(\tau) + \cdots, \tag{4}$$

$$q(\tau,\epsilon) = q_0(\tau) + \epsilon q_1(\tau) + \epsilon^2 q_2(\tau) + \cdots. \tag{5}$$

The expansion of exp $(-q(\tau,\epsilon))$ in a Taylor series leads to

$$\exp(-q(\tau,\epsilon)) = \exp(-q(\tau,0)) + (\partial \exp(-q(\tau,\epsilon))/\partial\epsilon) \mid_{\epsilon=0} \epsilon$$
$$+ (1/2)(\partial^2 \exp(-q(\tau,\epsilon))/\partial\epsilon^2) \mid_{\epsilon=0} \epsilon^2 + \cdots,$$

which, by combining with Eq. (5) reduces to

$$\exp(-q(\tau,\epsilon)) = \exp(-q_0(\tau)) - \exp(-q_0(\tau))q_1(\tau)\epsilon$$
$$+ \exp(-q_0(\tau))[(1/2)q_0{}^2(\tau) - q_1(\tau)]\epsilon^2 + \cdots. \tag{6}$$

Substituting Eqs. (4)-(6) into Eq. (3), we obtain

$$dp_0(\tau)/d\tau + \epsilon dp_1(\tau)/d\tau + \epsilon^2 dp_2(\tau)/d\tau + \cdots = [1 - p_0(\tau)$$
$$- \epsilon p_1(\tau) - \cdots][\exp(-q_0(\tau)) - \epsilon \exp(-q_0(\tau))q_1(\tau) + \cdots],$$

$$dq_0(\tau)/d\tau + \epsilon dq_1(\tau)/d\tau + \epsilon^2 dq_2(\tau)/d\tau + \cdots = \epsilon p_0(\tau) + \epsilon^2 p_1(\tau)$$
$$+ \epsilon^3 p_2(\tau) + \cdots. \tag{7}$$

Setting the corresponding terms in ϵ equal, a series of differential equations is obtained which, successively solved, yields $p_0, p_1, \ldots,$ and $q_0, q_1, \ldots,$ respectively, with the initial conditions $p_n(0) = 0$ and $q_n(0) = 0$ (see Appendix 1):

$$q_0(\tau) = 0, \tag{8}$$

$$p_0(\tau) = 1 - \exp(-\tau), \tag{9}$$

$$q_1(\tau) = \tau + \exp(-\tau) - 1, \tag{10}$$

$$p_1(\tau) = [\exp(-\tau) - (1/2)\tau^2 + \tau - 1]\ \exp(-\tau), \tag{11}$$

$$q_2(\tau) = -(1/2)[1 + \exp(-\tau)(\exp(-\tau) - \tau^2 - 2)]. \tag{12}$$

The first approximation of $q(\tau,\epsilon)$ is taken as

$$q_{\mathrm{I}}(\tau,\epsilon) = \epsilon(\tau + \exp(-\tau) - 1), \tag{13}$$

and the second approximation as

$$q_{\mathrm{II}}(\tau,\epsilon) = \epsilon(\tau + \exp(-\tau) - 1) - (1/2)\epsilon^2\,[1 + \exp(-\tau)(\exp(-\tau) - \tau^2 - 2)]. \tag{14}$$

To compare the approximations with the "accurate" solution of Set (3), the set was numerically integrated with a Runge-Kutta routine for ϵ ranging from 0.1 to 1 and monomer conversions up to 95%. The results, presented in Fig. 1 as first-order plots, show that, as expected, the predictions of the approximate solutions diverge increasingly from the numerical solution with increasing conversion. For $\epsilon = 0.1$, all three solutions are virtually identical up to monomer conversions above 95%. The dependence of relative error on conversion and on ϵ is illustrated in Fig. 2, which confirms the superior accuracy of the second approximation.

In terms of real time, the two approximations may be written as follows:

$$q_{\mathrm{I}}(t) = k_p[\mathrm{I}]_0 t + (k_p[\mathrm{I}]_0/(k_i[\mathrm{M}]_0))(\exp(-k_i[\mathrm{M}]_0 t) - 1), \tag{15}$$

$$\begin{aligned} q_{\mathrm{II}}(t) = {} & k_p[\mathrm{I}]_0 t + (k_p[\mathrm{I}]_0/(k_i[\mathrm{M}]_0))(\exp(-k_i[\mathrm{M}]_0 t) - 1) \\ & - (1/2)(k_p[\mathrm{I}]_0/(k_i[\mathrm{M}]_0))^2\{1 + [\exp(-k_i[\mathrm{M}]_0 t) - (k_i[\mathrm{M}]_0 t)^2 - 2] \\ & \exp(-k_i[\mathrm{M}]_0 t)\}. \end{aligned} \tag{16}$$

Both functions at infinity approach asymptotes of slope $k_p[\mathrm{I}]_0$; the asymptote of $q_{\mathrm{I}}(t)$ is

$$y_{\mathrm{I}}(t) = k_p[\mathrm{I}]_0 t - k_p[\mathrm{I}]_0/(k_i[\mathrm{M}]_0) \tag{17}$$

and that of $q_{\mathrm{II}}(t)$ is

$$y_{\mathrm{II}}(t) = k_p[\mathrm{I}]_0 t - k_p[\mathrm{I}]_0/(k_i[\mathrm{M}]_0) - 0.5\,[k_p[\mathrm{I}]_0/(k_i[\mathrm{M}]_0)]^2. \tag{18}$$

As pointed out by Litt [1] and Pepper [8], the actual slope of the asymptote of q is $k_p[\mathrm{I}]_0 f$, where f is the value of p at infinity and can be calculated by solving the equation

$$-\ln(1-f)-f=1/\epsilon. \tag{19}$$

Since f gets closer to unity as ϵ tends toward zero, the agreement of the exact solution of the Set (2) with q_I and q_II becomes increasingly better the smaller the value of ϵ. This also implies that the usual method of finding k_p from the final slope of $a(-\ln(1-x))$ vs time plots gives good approximations of k_p only when ϵ is small [8].

For approximating k_i, we start from the fact that, for small ϵ's, the slopes of the asymptotes of q_II and q tend to become equal and also that the derivatives of q_II and q become relatively soon (at low conversions) almost equal with the slopes of the respective asymptotes. It follows that the two asymptotes are, at least for the initial portion of the curves, very close to each other; hence, their intercepts on the abscissa are also close. The above reasoning applies for q_I as well, if $\epsilon < 0.1$.

The intercepts of the asymptotes of q_I and q_II are

$$t_1 = 1/(k_i[\mathrm{M}]_0), \tag{20}$$

$$t_2 = 1/(k_i[\mathrm{M}]_0) + 0.5k_p[\mathrm{I}]_0/(k_i[\mathrm{M}]_0). \tag{21}$$

Hence, as $t_1 \approx t_2 \approx t_0$ ($t_0 \equiv$ the intercept of the asymptote of q),

$$k_i \approx 1/(t_0[\mathrm{M}]_0) \equiv k_i^{\mathrm{I}} \tag{22}$$

$$k_i \approx [1 + (1 + 2t_0 k_p[\mathrm{I}]_0)^{1/2}]/(2t_0[\mathrm{M}]_0) \equiv k_i^{\mathrm{II}}. \tag{23}$$

Mention should be made that Eq. (22) has been previously derived [12] by implicitly assuming constant monomer concentration during propagation. This assumption is chemically untenable and also leads to an incorrect mathematical treatment.

In order to determine t_0 from experimental data, the following methods can be used: (a) If the first-order plot of q shows an extended linear portion, linear regression may be applied, approximating t_0 as the intercept of the obtained straight line. (b) Data may be fitted with a function of properties similar to $-\ln(1-x)$, i.e., passing through the origin, increasing, convex, and approaching an asymptote as $t \to \infty$. The intercept on the abscissa of the asymp-

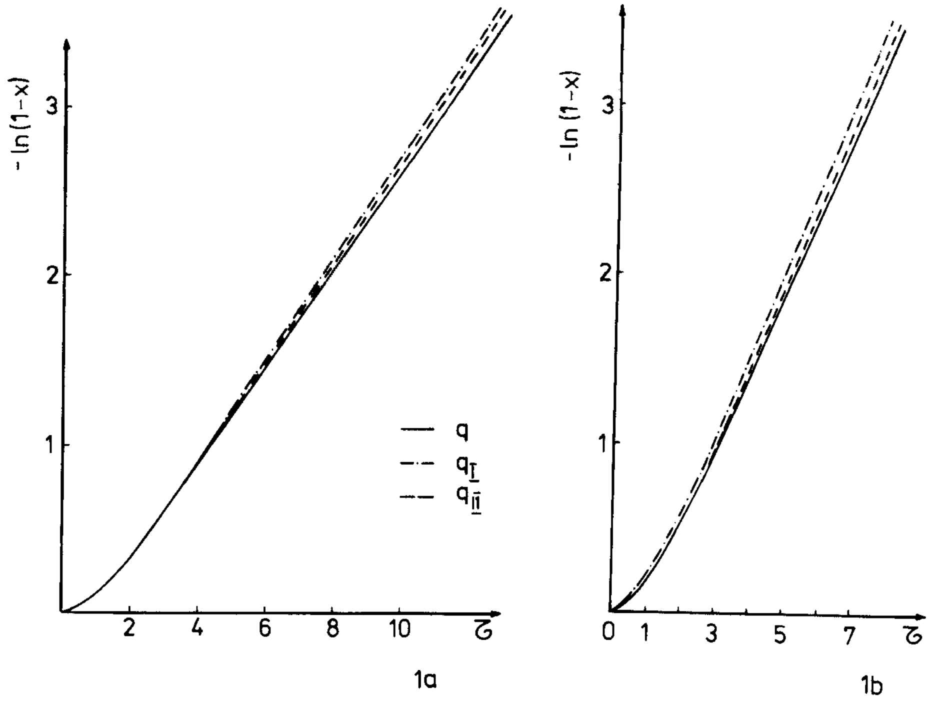

FIG. 1. Plots of the functions q (= -ln (1 - x), where x is the monomer conversion), q_{I}, and q_{II} for three values of ϵ: (a) $\epsilon = 0.3$, (b) $\epsilon = 0.5$, (c) $\epsilon = 0.9$.

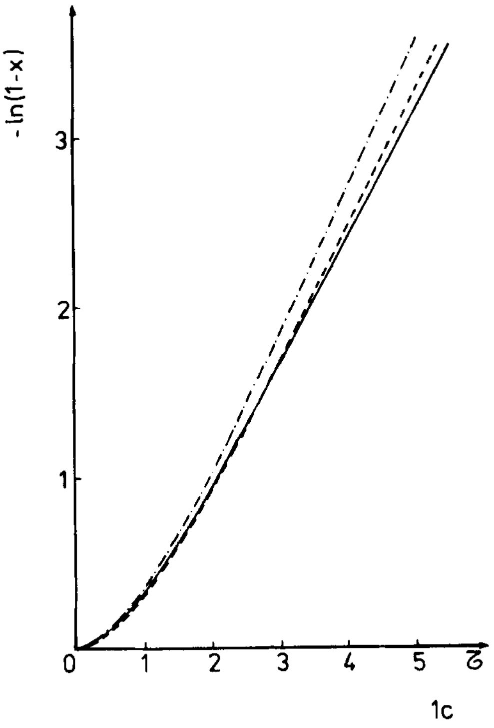

FIG. 1 (continued)

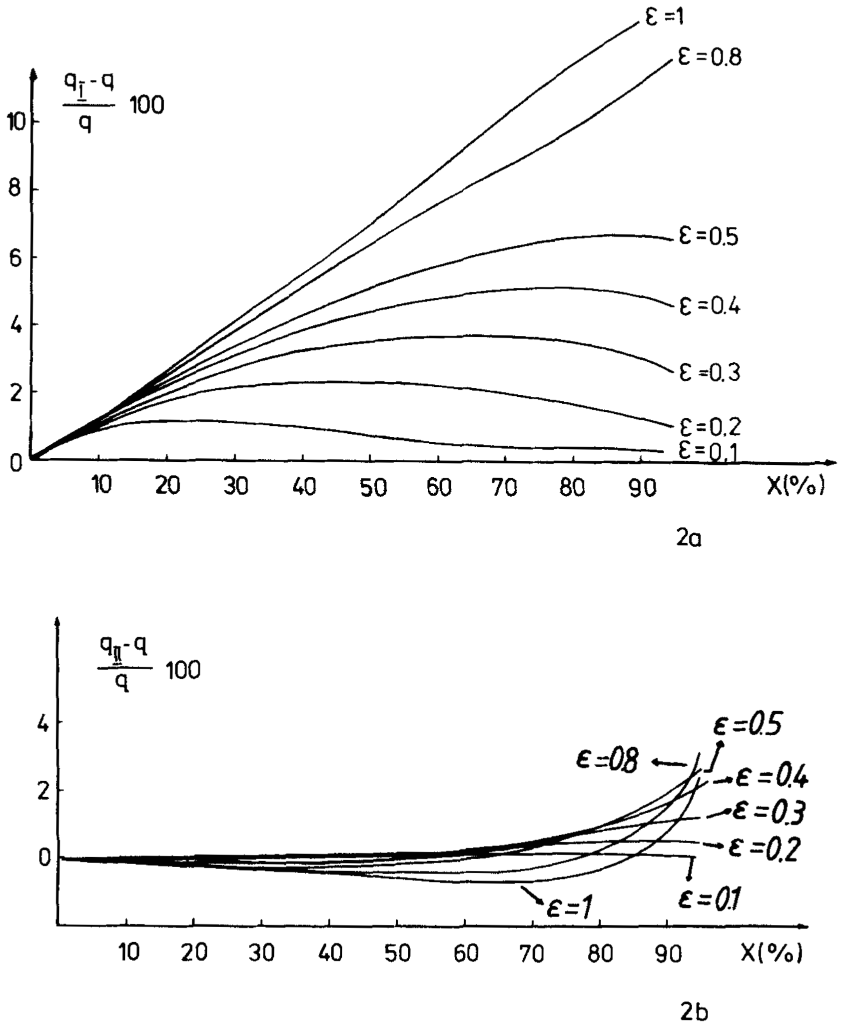

FIG. 2. Relative error of functions q_I and q (Fig. 2a) and of functions q_{II} and q (Fig. 2b) for some values of ϵ ranging from 0.1 to 1.

tote of that function will approximate t_0. For this procedure we have rather arbitrarily chosen a hyperbolic branch with the apex at the origin:

$$y(t) = -a + (a/b)(t^2 + b^2)^{1/2} \tag{24}$$

and the function

$$y(t) = \alpha t^2/(t + \beta). \tag{25}$$

The problem is that, for unknown k_i and k_p, one cannot evaluate ϵ a priori, so that the question arises whether Eqs. (15) and (16) derived for $\epsilon < 1$ are usable or not. However, it can be shown that the same equations are valid even if $\epsilon > 1$. The mathematical treatment is rather complicated and is presented only schematically in Appendix 2. More precisely, it can be shown that, for any ϵ, a conversion interval exists in which Eq. (16) constitutes a good approximation of the exact solution $q(t)$ at a given degree of precision. The maximum monomer conversion for which this approximation still holds decreases with increasing ϵ. Even for $\epsilon \gg 1$, this conversion is relatively high. Thus, for $\epsilon = 1000$ the relative error is less than 5% for conversions up to 60% (Fig. 3). In practice, such large values of ϵ are seldom encountered (solving

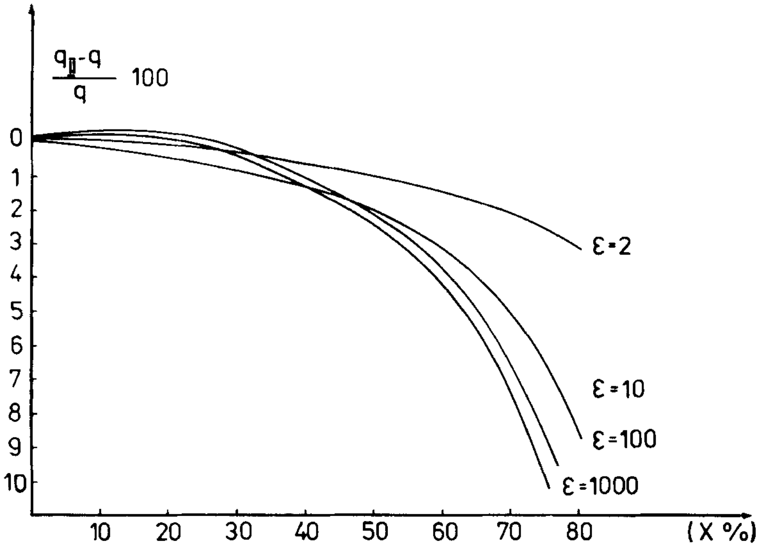

FIG. 3. Relative error of functions q_{II} and q for very high values of ϵ.

Eq. 19 for $\epsilon = 1000$ gives $f < 0.04$, which means that the initiator consumption is less than 4%).

In general, the following method is to be applied: The experimental data obtained in a polymerization are treated as above to determine k_p and k_i. If these values lead to small standard deviations of q_{II} from the experimental points, then they are by themselves good approximations for the reaction rate constants. If not, it follows that ϵ is very large and the obtained values for k_p and k_i should be regarded as indicating only the order of magnitude of the actual rate constants. The knowledge of these orders of magnitude will enable the researcher to choose the ratio $[I]_0/[M]_0$ required to obtain a small ϵ $(= k_p[I]_0/(k_i[M]_0))$. With these initial concentrations, a second polymerization is performed, from whose results good approximations for k_p and k_i will be obtained.

However, if only one set of experimental data is available and ϵ is very large, one can still determine the rate constants by computer fitting of the data with function q_{II} (much faster than fitting with a numerical solution). The computer fitting method has the further advantage of yielding values for k_p much more accurate than those obtained from the final slope.

Since, for $\epsilon \gg 1$, problems related to the shape of the function q_{II} arise, in this case one should fit with q_{II} only data corresponding to monomer conversions below 75%.

APPLICATION TO EXPERIMENTAL DATA

In order to estimate the degree of approximation when k_i is calculated with Eqs. (22) and (23), the cationic polymerization of *N*-vinylcarbazole initiated with triphenylmethyl hexafluoroantimonate was considered. For this reaction at 20°C, $k_i = 130\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $k_p = 5 \times 10^4\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ [13].

Set (2) was numerically integrated for $[M]_0 = 0.04\ \text{mol}\cdot\text{L}^{-1}$ and variable $[I]_0$ corresponding to $\epsilon = 0.1, \ldots, 1$; $\epsilon = 2$; and $\epsilon = 10$. The results were used to obtain, by linear regression and fitting with the Functions (24) and (25), the intercept t_0 which was substituted in (22) and (23) to provide the approximate values for k_i (k_i^{I} and k_i^{II}). These are presented in Table 1, k_p being calculated from the final slope. For small values of ϵ, the various k_i^{I} and k_i^{II} values are very close to each other. For high values of ϵ, there are great differences between these constants, and it is necessary to select the best approximation for k_i from among them. In order to do this, we substitute the constants k_p and k_i^{I} in q_I and k_p and k_i^{II} in q_{II} and calculate

TABLE 1. Approximate Values of k_p and k_i Obtained by Processing the Data Resulting from Numerical Integration of Set (2) with k_p = 50 000 L•mol^{-1}•s^{-1} and k_i = 130 L•mol^{-1}•s^{-1}

	Linear regression			Fitting with Function (24)			Fitting with Function (25)		
ϵ	k_p	k_i^{I}	k_i^{II}	k_p	k_i^{I}	k_i^{II}	k_p	k_i^{I}	k_i^{II}
0.1	50 020	121	127	50 076	115	122	50 171	109	115
0.2	49 787	118	129	50 062	105	117	50 401	94	105
0.3	48 986	123	140	49 562	103	120	50 276	86	103
0.4	47 928	128	148	48 723	104	125	50 095	83	104
0.5	46 084	145	170	47 646	108	133	48 528	90	114
0.6	44 779	153	183	46 537	112	141	48 120	87	115
0.7	43 596	163	195	45 416	116	148	48 609	80	112
0.8	42 734	166	202	44 431	120	156	47 801	82	116
0.9	41 474	176	215	43 478	123	162	46 851	84	121
1	40 808	178	215	42 587	126	168	45 658	87	128
2	33 212	241	308	35 900	157	223	40725	92	155
10	17 020	573	744	20 417	303	473	27 178	135	279

the standard deviation of q_{I} and q_{II} from the experimental data. We select k_p and k_i which minimize the standard deviation.

We illustrate this method by the treatment of the data reported by Pepper and Ryan [14] on the polymerization of butyl cyanoacrylate with Ph_3P in THF at 20°C ($[M]_0$ = 0.0065 mol•L^{-1}, $[I]_0$ = 2.6 × 10^{-6} mol•L^{-1}). The hyperbola gave the best fit, yielding k_p = 2.8 × 10^5 L•mol^{-1}•s^{-1} and k_i = 104 L•mol^{-1}•s^{-1}, for which the standard deviation was σ = 0.062 (see Fig. 4).

To test the method of fitting the data with q_{II}, we used the results of the numerical integration of Set (2) with k_p = 50 000 L•mol^{-1}•s^{-1}, k_i = 130 L•mol^{-1}•s^{-1}, $[M]_0$ = 0.04 mol•L^{-1}, and $[I]_0$ selected to get ϵ = 10 (a very

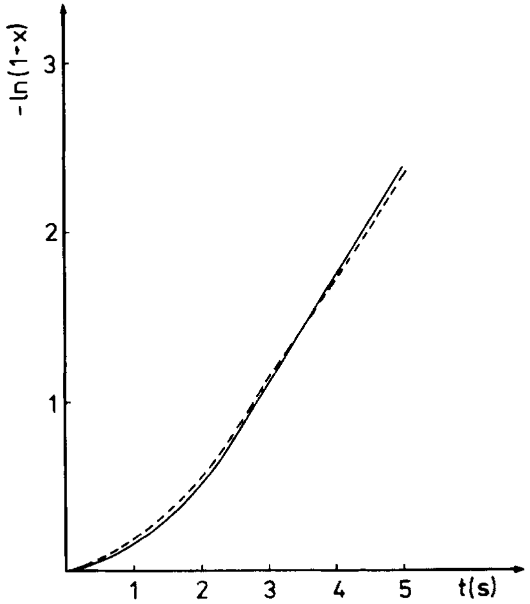

FIG. 4. Experimental curve (——) obtained for the polymerization of butyl cyanoacrylate with Ph_3P in THF at 20°C [14] compared to the second-order approximation, q_{II} (– –).

large ϵ). As starting values for the fitting program we used k_p = 20 417 $L \cdot mol^{-1} \cdot s^{-1}$ and k_i = 473 $L \cdot mol^{-1} \cdot s^{-1}$, which were chosen rather arbitrarily from those in the last row of Table 1. The values yielded by the fitting program were k_p = 56 030 $L \cdot mol^{-1} \cdot s^{-1}$ and k_i = 116 $L \cdot mol^{-1} \cdot s^{-1}$.

CONCLUSIONS

For usual values of ϵ, the approximate solutions we have derived are in good agreement with that obtained by numerical integration; hence the calculated constants are close to their actual values. Even when ϵ is unusually large, both constants k_p and k_i may be determined by computer fitting of experimental data with the second-order approximate analytical solution.

APPENDIX 1

Set (7) can be written

$$dp_0(\tau)/d\tau + \epsilon dp_1(\tau)/d\tau + \epsilon^2 dp_2(\tau)/d\tau + \cdots = [1 - p_0(\tau)] \exp(-q_0(\tau))$$
$$- \epsilon [(1 - p_0(\tau))q_1(\tau) \exp(-q_0(\tau)) + p_1(\tau) \exp(-q_0(\tau))] + \cdots,$$

$$dq_0(\tau)/d\tau + \epsilon dq_1(\tau)/d\tau + \epsilon^2 dq_2(\tau)/d\tau + \cdots = \epsilon p_0(\tau)$$
$$+ \epsilon^2 p_1(\tau) + \cdots. \qquad \text{(A1.1)}$$

The initial conditions for p_n and q_n are $p_n(0) = 0$ and $q_n(0) = 0$ for any $n \in N$.

From Relation $(\text{A1.1})_2$, by equating the free terms it follows that

$$dq_0(\tau)/d\tau = 0,$$

which, together with the initial condition, gives

$$q_0(\tau) = 0. \qquad \text{(A1.2)}$$

By the same method, from $(\text{A1.1})_1$, we obtain

$$dp_0(\tau)/d\tau = (1 - p_0(\tau)) \exp(-q_0(\tau)).$$

(A1.2) and the initial conditions for p_0 are used to get

$$p_0(\tau) = 1 - \exp(-\tau). \qquad \text{(1.3)}$$

Identifying the ϵ terms in $(\text{A1.1})_2$, we come to

$$dq_1(\tau)/d\tau = p_0(\tau),$$

and

$$q_1(\tau) = \tau + \exp(-\tau) - 1. \qquad \text{(A1.4)}$$

The same procedure applied to Eq. $(\text{A1.1})_1$ leads to

$$dp_1(\tau)/d\tau = -(1 - p_0(\tau))q_1(\tau) \exp(-q_0(\tau)) - p_1(\tau) \exp(-q_0(\tau)).$$

After performing the necessary substitutions and solving the differential equation, we get

$$p_1(\tau) = [\exp(-\tau) - 0.5\tau^2 + \tau - 1] \exp(-\tau). \qquad \text{(A1.5)}$$

By equating the ϵ^2 terms in $(\text{A1.1})_2$, the equation

$$dq_2(\tau)/d\tau = p_1(\tau)$$

is obtained and it follows that

$$q_2(\tau) = -1/2[1 + (\exp(-\tau) - \tau^2 - 2)\exp(-\tau)]. \qquad \text{(A1.6)}$$

APPENDIX 2

Set (2) is rendered dimensionless by using instead of the actual time t, the dimensionless time $\bar{\tau} = k_i[\text{I}]_0 t$. With $\mu = [\text{I}]_0/[\text{M}]_0$, the set becomes

$$\mu dp/d\bar{\tau} = (1 - p)\exp(-q),$$

$$dq/d\bar{\tau} = (k_p/k_i)p.$$

Since normally $\mu << 1$, the problem may be solved by the method of singular perturbations [11]. The process by which the approximate solution is found is rather tedious, and since it closely follows the general algorithm persented in Ref. 11, we shall not present it here. Suffice it to say that the second approximation of q obtained by this method is

$$q_{\text{II}} = (k_p/k_i)\bar{\tau} + \mu(k_p/k_i)(\exp(-\tau) - 1) + \mu^2(k_p/k_i)^2(-1/2)[1 + (\exp(-\tau) - \tau^2 - 2)\exp(-\tau)],$$

where $\tau = \bar{\tau}/\mu = k_i[\text{M}]_0 t$.

Substituting for real time, one obtains Eq. (16).

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