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### An Approximate Kinetic Treatment of Slow-Initiated Living Polymerization. II. First-Order Initiation and Half-Order Propagation

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

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### ABSTRACT

An approximate analytical solution of the set of differential equations modeling the anionic polymerization of styrene is presented. By using this solution, a new method for calculating the initiation rate constant for this polymerization process was developed.

### INTRODUCTION

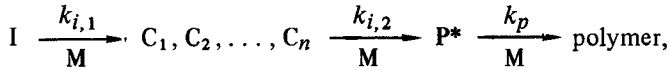
In our previous paper [1] we presented a method for approximating the initiation rate constant for a slow-initiated living polymerization in which both initiation and propagation are first order with respect to all participants. Following the same mathematical reasoning, we shall now treat the case of the anionic polymerization of styrene, initiated with *n*-butyllithium, in which the propagation is half order with respect to the active centers.

### THEORY

It has been established [2, 3] that, in styrene polymerization with *n*-butyllithium in aromatic hydrocarbons, the first stage of initiation is the formation of aggregates of reaction products between alkylolithium and monomer. It is

assumed that, upon reaching a critical size, the intermediate aggregates become available for initiation proper, i.e., for the formation of centers active in subsequent propagation.

The kinetics of this polymerization process is described by



where I represents the initiator,  $C_1$  to  $C_n$  are secondary aggregates of increasing size and decreasing reactivity,  $P^*$  represents active chains, and M represents monomer molecules. The corresponding set of differential equations is

$$\begin{aligned} d[I]/dt &= -k_{i,1} [I] [M], \\ d[C]/dt &= (k_{i,1} [I] - k_{i,2} [C]) [M], \\ d[P^*]/dt &= k_{i,2} [C] [M], \\ d[M]/dt &= -k_p [P^*]^{1/2} [M], \end{aligned} \quad (1)$$

with the initial conditions  $[I] |_{t=0} = [I]_0$ ,  $[C] |_{t=0} = 0$ ,  $[P^*] |_{t=0} = 0$ ,  $[M] |_{t=0} = [M]_0$ .

The value of  $k_{i,1}$  can easily be determined experimentally by spectrophotometric measurements [2].

The inequality  $k_{i,1} \gg k_{i,2}$  holds, leading to a very rapid consumption of the initiator, whose concentration tends toward zero in a time interval  $[0, t')$  during which  $[M]$  and  $[P^*]$  do not show any noticeable transformations [3]. We shall consider the set obtained from Set (1) after the consumption of the initiator by neglecting the time interval  $[0, t')$  and the monomer and active centers variation during this time interval,

$$\begin{aligned} d[P^*]/dt &= k_{i,2} ([I]_0 - [P^*]) [M], \\ d[M]/dt &= -k_p [P^*]^{1/2} [M], \end{aligned} \quad (2)$$

with the initial conditions  $[P^*] |_{t=0} = 0$ ,  $[M] |_{t=0} = [M]_0$  (we have used the obvious relation  $[I] + [C] + [P^*] = [I]_0$ ).

With the dimensionless variables  $m = [M]/[M]_0$ ,  $p = [P^*]/[I]_0$ , and  $\tau = k_{i,2} [M]_0 t$ , we get to

$$\begin{aligned} dp/d\tau &= (1 - p)m, \\ dm/d\tau &= -(k_p [I]_0^{1/2})/(k_{i,2} [M]_0) p^{1/2} m, \end{aligned} \tag{3}$$

which, by considering the dimensionless parameter  $\epsilon = k_p [I]_0^{1/2} / (k_{i,2} [M]_0)$  and the substitution  $q(\tau) = -\ln m(\tau)$ , becomes

$$\begin{aligned} dp/d\tau &= (1 - p) \exp(-q), \\ dq/d\tau &= \epsilon p^{1/2}, \end{aligned} \tag{4}$$

$$p \big|_{\tau=0} = 0, q \big|_{\tau=0} = 0.$$

We shall first consider the case  $\epsilon < 1$ , and we shall apply the theory of regular perturbations [4]. It can be shown that the solutions of Set (4) (which are functions of both  $\tau$  and  $\epsilon$ ) accept partial derivatives of third order with respect to  $\epsilon$ , allowing us to look for second-order approximations of these solutions. Hence, we shall expand the functions  $p$  and  $q$  in a power series of  $\epsilon$ :

$$\begin{aligned} p(\tau, \epsilon) &= p_0(\tau) + \epsilon p_1(\tau) + \epsilon^2 p_2(\tau) + \dots, \\ q(\tau, \epsilon) &= q_0(\tau) + \epsilon q_1(\tau) + \epsilon^2 q_2(\tau) + \dots, \end{aligned}$$

and we shall use the expansions of  $\exp(-q(\tau, \epsilon))$  [1] and of  $p(\tau, \epsilon)^{1/2}$  in a power series of  $\epsilon$ :

$$\begin{aligned} p(\tau, \epsilon)^{1/2} &= p(\tau, 0)^{1/2} + \partial(p(\tau, \epsilon)^{1/2})/\partial\epsilon \big|_{\epsilon=0} \\ &+ (1/2)\partial^2(p(\tau, \epsilon)^{1/2})/\partial\epsilon^2 \big|_{\epsilon=0}\epsilon^2 + \dots, \end{aligned}$$

i.e.,

$$p(\tau, \epsilon)^{1/2} = p_0(\tau)^{1/2} + (1/2)p_0(\tau)^{-1/2}p_1(\tau)\epsilon + \dots.$$

We obtain the set

$$\begin{aligned} dp_0(\tau)/d\tau + \epsilon dp_1(\tau)/d\tau + \epsilon^2 dp_2(\tau)/d\tau + \dots &= (1 - p_0(\tau) - \epsilon p_1(\tau) \\ &- \dots) (\exp(-q_0(\tau)) - \epsilon q_1(\tau) \exp(-q_0(\tau)) + \dots), \\ dq_0(\tau)/d\tau + \epsilon dq_1(\tau)/d\tau + \epsilon^2 dq_2(\tau)/d\tau + \dots &= \epsilon p_0(\tau)^{1/2} \\ &+ \epsilon^2 (1/2)p_0(\tau)^{-1/2}p_1(\tau) + \dots. \end{aligned} \tag{5}$$

By equating the corresponding  $\epsilon$  terms in the above set, we obtain a series of differential equations from which the functions  $q_0, q_1, \dots$  and  $p_0, p_1, \dots$  will be calculated. The initial conditions for these equations are  $q_n(0) = 0$  for  $n \geq 0$  and  $p_n(0) = 0$  for  $n \geq 1$ . Since  $p_0$  has a negative exponent in the second equation of Set (5), we shall use an initial condition for this function of the form  $\lim_{\tau \rightarrow 0} p_0(\tau) = 0$ .

The functions  $p_n$  and  $q_n$  are (see the Appendix)

$$q_0(\tau) = 0, \quad (6)$$

$$p_0(\tau) = 1 - \exp(-\tau), \quad (7)$$

$$q_1(\tau) = \tau - 2(1 - \exp(-\tau))^{1/2} + 2 \ln[1 + (1 - \exp(-\tau))^{1/2}], \quad (8)$$

$$p_1(\tau) = -\exp(-\tau) \int_0^\tau q_1(s) ds, \quad (9)$$

$$\begin{aligned} q_2(\tau) = & -0.5\tau^2 [(1 - \exp(-\tau))^{1/2} - 1] + 2\tau \ln[1 + (1 - \exp(-\tau))^{1/2}] \\ & - 2(1 - \exp(-\tau))^{1/2} \int_0^\tau \ln[1 + (1 - \exp(-s))^{1/2}] ds - 2(1 - \exp(-\tau)) \\ & + 2 \ln^2 [1 + (1 - \exp(-\tau))^{1/2}]. \end{aligned} \quad (10)$$

The first-order approximation of the function  $q(\tau, \epsilon)$  is

$$q_I(\tau, \epsilon) = \epsilon q_1(\tau), \quad (11)$$

and the second-order approximation is

$$q_{II}(\tau, \epsilon) = \epsilon q_1(\tau) + \epsilon^2 q_2(\tau). \quad (12)$$

By using Relations (8) and (10) and by substituting the expression of  $\tau (= k_{i,2} [M]_0 t)$  and that of  $\epsilon (= k_p [I]_0^{1/2} / (k_{i,2} [M]_0))$  in Eqs. (11) and (12), we obtain  $q_I$  and  $q_{II}$  as functions of the actual time  $t$  of the initial concentrations and of the reaction rate constants.

To compare the two approximations with the exact solution of Set (1), we have numerically integrated this set of differential equations with the constants  $k_{i,1} = 5.814 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ ,  $k_{i,2} = 0.075 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ ,  $k_p = 0.131 \text{ L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{min}^{-1/2} \cdot \text{mol}^{-1/2} \cdot \text{min}^{-1}$ ,  $[M]_0 = 0.6 \text{ mol} \cdot \text{L}^{-1}$ , and vari-

able  $[I]_0$  so as to obtain  $\epsilon = 0.1, \epsilon = 0.2, \dots, \epsilon = 0.7$ . Plots of the three functions are presented in Fig. 1 for three values of  $\epsilon$ .

In a plot of the relative error vs conversion (Fig. 2), an increase of this error at very small conversions is observed, due to the approximation implied by going from Set (1) to Set (2). Since, at very small conversions, the function  $q$  ( $= -\ln(1-x)$ , where  $x$  is the monomer conversion) is very small, though the relative error may seem large, the values of  $q$  and  $q_{II}$  are very close to each other.

As  $t$  tends to infinity, the functions  $q_I$  and  $q_{II}$  approach asymptotes

$$y_I(t) = k_p [I]_0^{1/2} t - [k_p [I]_0^{1/2} / (k_{i,2} [M]_0)] 2(1 - \ln 2) \quad (13)$$

and

$$y_{II}(t) = k_p [I]_0^{1/2} t - [k_p [I]_0^{1/2} / (k_{i,2} [M]_0)] 2(1 - \ln 2) - 2[k_p [I]_0^{1/2} / (k_{i,2} [M]_0)]^2 (1 - \ln^2 2 - \alpha), \quad (14)$$

where

$$\alpha = \lim_{\tau \rightarrow \infty} \left\{ \tau \ln [1 + (1 - \exp(-\tau))^{1/2}] - (1 - \exp(-\tau))^{1/2} \int_0^\tau \ln [1 + (1 - \exp(-s))^{1/2}] ds \right\}. \quad (15)$$

It can be shown that  $\alpha \approx 0.34$ .

We observe that, as  $t \rightarrow \infty$ , the functions  $q_I$  and  $q_{II}$  diverge from  $q$ , since the asymptotes  $y_I$  and  $y_{II}$  have slopes equal to  $k_p [I]_0^{1/2}$  and the asymptote of  $q$  has the slope  $k_p [I]_0^{1/2} f^{1/2}$ , where  $f$  is the final value of  $p$  ( $f = \lim_{\tau \rightarrow \infty} p(\tau)$ ).

The equation (similar to Litt's equation [5]) that yields the value of  $f$  can be obtained by dividing Eq. (3)<sub>2</sub> by Eq. (3)<sub>1</sub> and integrating:

$$(1 - m)/\epsilon = \ln(1 + p^{1/2}) / (1 - p^{1/2}) - 2p^{1/2}. \quad (16)$$

As  $t \rightarrow \infty$ ,  $m$  tends toward zero, hence

$$\ln(1 + f^{1/2}) / (1 - f^{1/2}) - 2f^{1/2} = 1/\epsilon, \quad (17)$$

from which  $f$  may be found. For small  $\epsilon$ 's,  $f \approx 1$ , but when  $\epsilon$  increases,  $f$  tends toward zero (see Table 1). It follows that the smaller  $\epsilon$  is, the better will be the agreement of  $q_I$  and  $q_{II}$  with  $q$ .

In order to approximate  $k_{i,2}$ , we shall now consider the intercepts of the two asymptotes  $y_I$  and  $y_{II}$  on the abscissa:

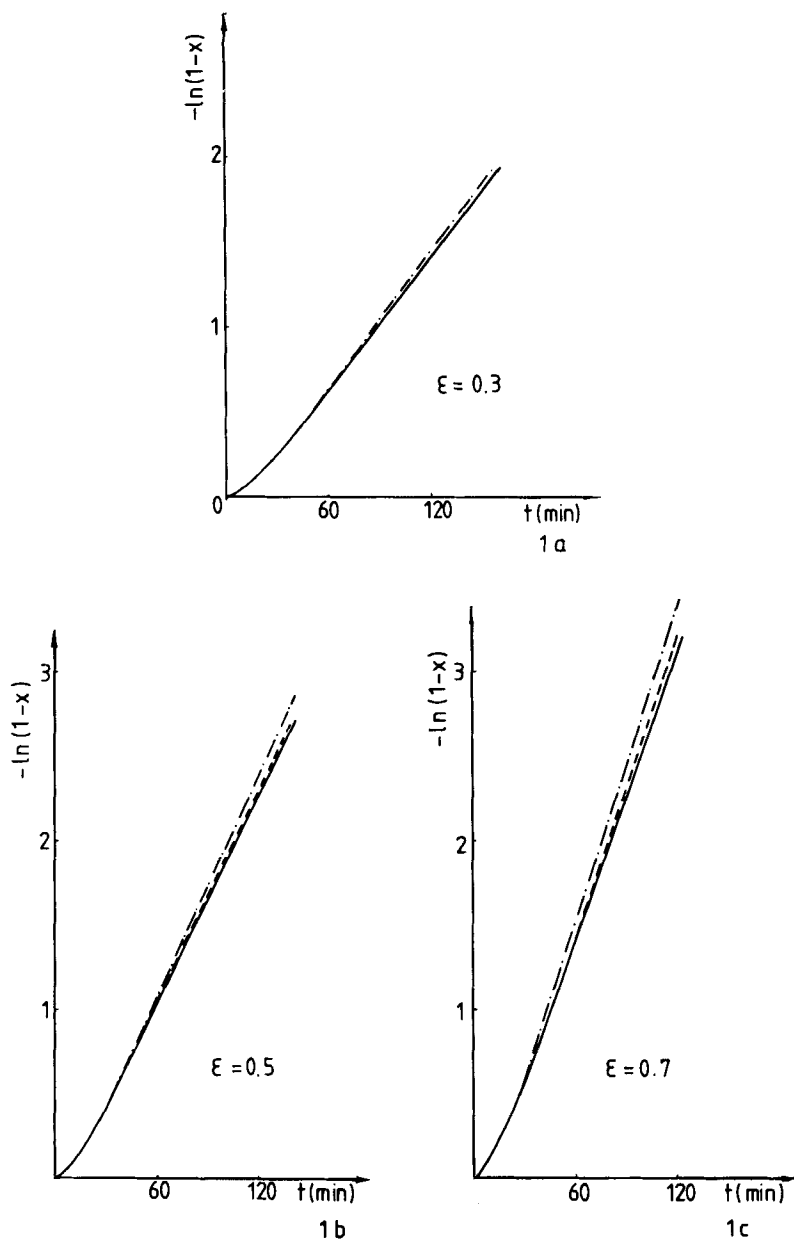


FIG. 1. Plots of the function  $q$  ( $= -\ln(1-x)$ , where  $x$  is the monomer conversion) and of the two approximations for three values of  $\epsilon$ :  $q$  (—),  $q_I$  (- · -),  $q_{II}$  (- - -). For  $\epsilon = 0.3$ ,  $q$  and  $q_{II}$  are superimposed.

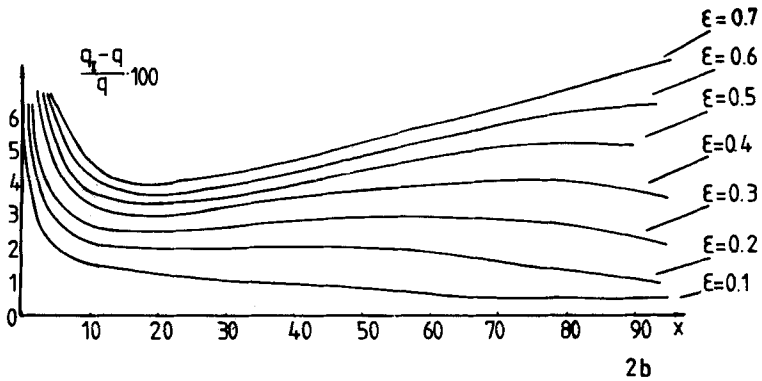
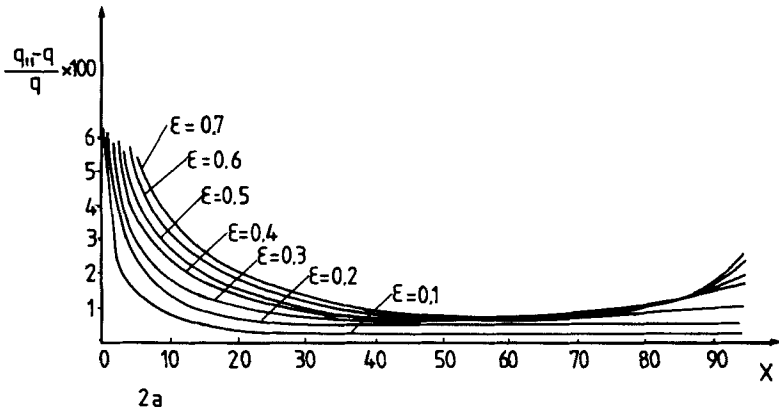


FIG. 2. Relative error of the functions  $q$  and  $q_{II}$  (a), and  $q$  and  $q_I$  (b)



TABLE 1. Final Value of  $f$  as a Function of  $\epsilon$ 

$\epsilon$	$f$	$\epsilon$	$f$
0.1	0.999	0.7	0.860
0.2	0.996	0.8	0.830
0.3	0.980	0.9	0.802
0.4	0.954	1	0.776
0.5	0.923	2	0.592
0.6	0.891	10	0.252

$$t_1 = 2(1 - \ln 2)/(k_{i,2} [M]_0) \quad (18)$$

and

$$t_2 = 2(1 - \ln 2)/(k_{i,2} [M]_0) + [2k_p [I]_0^{1/2}/(k_{i,2} [M]_0)^2](1 - \ln^2 2 - \alpha). \quad (19)$$

These simple equations lead to

$$k_{i,2} = 2(1 - \ln 2)/(t_1 [M]_0) \quad (20)$$

$$= \left\{ 1 - \ln 2 + [(1 - \ln 2)^2 + 2(1 - \alpha - \ln^2 2)k_p [I]_0^{1/2} t_2]^{1/2} \right\} / (t_2 [M]_0) \quad (21)$$

By assuming that  $t_1$  and  $t_2$  are very

By assuming that  $t_1$  and  $t_2$  are very close to the intercept  $t_0$  of the asymptote of the exact solution (i.e.,  $t_1 \approx t_2 \approx t_0$ ), we obtain the following approximate equations for  $k_{i,2}$ :

$$k_{i,2}^I = 2(1 - \ln 2)/(t_0 [M]_0), \quad (22)$$

$$k_{i,2}^{II} = \left\{ 1 - \ln 2 + [(1 - \ln 2)^2 + 2(1 - \alpha - \ln^2 2)k_p [I]_0^{1/2} t_0]^{1/2} \right\} / (t_0 [M]_0). \quad (23)$$

These equations will give good approximations of  $k_i$  for small values of  $\epsilon$ . However, it can be demonstrated by using another dimensionless time,  $\bar{\tau} = k_{i,2} [I]_0 t$ , and applying the theory of singular perturbations [4] that, even if

$\epsilon > 1$ , the function  $q_{II}$  is a good approximation for  $q$  in a certain time interval (the length of this time interval will decrease with increasing  $\epsilon$ ). If, in a certain polymerization,  $\epsilon$  has a very large value and, as a result, large differences are observed between  $q_{II}$  (calculated with  $k_p$  obtained from the final slope of a  $q$  vs time plot, and  $k_{i,2}$  obtained as above) and the experimental data, a second polymerization can be performed with  $[I]_0$  and  $[M]_0$  chosen so as to result in a small  $\epsilon$  (the  $k_p$  and  $k_{i,2}$  resulting from the previous polymerization will indicate the order of magnitude of the actual constants).

Both constants,  $k_p$  and  $k_{i,2}$ , may also be found by computer fitting of the experimental data with the function  $q_{II}$ . A serious impediment for this fitting is the presence in the expression of  $q_{II}$  of an integral that cannot be calculated analytically. However, this difficulty may be by-passed by finding a function to approximate this integral. On using the integration by parts formula several times, it can be shown that

$$\int_0^\tau \ln [1 + (1 - \exp(-s))^{1/2}] ds = \tau \ln [1 + (1 - \exp(-\tau))^{1/2}] + 0.5 \{ \ln [1 + (1 - \exp(-\tau))^{1/2}] \}^2 + [1 - (1 - \exp(-\tau))^{1/2}] - 1.5 \exp(-\tau) \ln [1 - (1 - \exp(-\tau))^{1/2}] / [1 + (1 - \exp(-\tau))^{1/2}]^2 - [7(1 - \exp(-\tau)) + 2(1 - \exp(-\tau))^{1/2}] / \{ 4[1 + (1 - \exp(-\tau))^{1/2}]^2 \} - I, \quad (24)$$

where (by putting  $B(\tau) = (1 - \exp(-\tau))^{1/2}$ )

$$I(\tau) = \int_0^{B(\tau)} [1.5s^2 - s - (s-1)^2 \ln(1-s)] / (1+s)^3 ds. \quad (25)$$

The maximal value of integral  $I$ , corresponding to  $\tau \rightarrow \infty$ , is less than 0.02 ( $\lim_{\tau \rightarrow \infty} I(\tau) = 0.0195$ ).

By neglecting the term  $I$  in Eq. (24) and by substituting the resulted relation in Eq. (10) and then in Eq. (12), we obtain, with the time  $t$  and the notation  $A(t) = 1 - \exp(-k_{i,2}[M]_0 t)$ :

$$q_{II}(t) = k_p [I]_0^{1/2} t + 2\epsilon \{ \ln [1 + A(t)^{1/2}] - A(t)^{1/2} \} + \epsilon^2 \{ 0.5 [1 - A(t)^{1/2}] [k_{i,2}[M]_0 t + 2 \ln(1 + A(t)^{1/2})]^2 + A(t)^{1/2} \ln^2(1 + A(t)^{1/2}) - [A(t)^{1/2} (3A(t) - 2A(t) - 2A(t)^{1/2} - 1) \ln(1 - A(t)^{1/2}) + 0.5A(t)(2 + A(t)^{1/2} + 4A(t))] / (1 + A(t)^{1/2})^2 \}. \quad (26)$$

TABLE 2. Values of  $k_p$  and  $k_{i,2}$  Obtained by Processing the Data Resulting from the Numerical Integration of Set (1) with  $k_{i,2} = 5.814 \text{ L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$ ,  $k_{i,2} = 0.075 \text{ L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$ ,  $k_{i,2} = 0.131 \text{ L}^{1/2}\cdot\text{mol}^{-1/2}\cdot\text{min}^{-1}$ , and  $[\text{M}]_0 = 0.6 \text{ mol}\cdot\text{L}^{-1}$

$\epsilon$	Linear regression			Fitting with a hyperbolic branch			Fitting with a rational function		
	$k_p$	$k_{i,2}^I$	$k_{i,2}^{II}$	$k_p$	$k_{i,2}^I$	$k_{i,2}^{II}$	$k_p$	$k_{i,2}^I$	$k_{i,2}^{II}$
0.1	0.1308	0.070	0.074	0.1313	0.064	0.068	0.1323	0.056	0.060
0.2	0.1303	0.067	0.075	0.1306	0.062	0.070	0.1314	0.056	0.063
0.3	0.1292	0.067	0.078	0.1295	0.062	0.073	0.1301	0.056	0.067
0.4	0.1267	0.073	0.087	0.1276	0.064	0.078	0.1279	0.058	0.072
0.5	0.1238	0.080	0.097	0.1252	0.068	0.085	0.1260	0.060	0.077
0.6	0.1215	0.084	0.104	0.1223	0.074	0.094	0.1239	0.063	0.082
0.7	0.1190	0.090	0.112	0.1198	0.080	0.102	0.1215	0.066	0.088

Although this formula is quite complex, fitting the data with it is much faster than fitting with a solution obtained by numerical integration. Moreover, for large values of  $\epsilon$ , the approximation of  $k_p$  obtained by fitting the data with Eq. (26) is much more accurate than that obtained by the classical method of dividing the final slope of  $q$  by  $[I]_0^{1/2}$  (since, as mentioned above, the actual final slope of  $q$  is not  $k_p [I]_0^{1/2}$  but  $k_p [I]_0^{1/2} f^{1/2}$ , where  $f$  tends toward zero as  $\epsilon$  increases).

### APPLICATION TO EXPERIMENTAL DATA

In order to see how the accuracy of the approximations of Eqs. (22) and (23) depends on  $\epsilon$ , we processed the data resulting from the integration of Set (1) (with constants  $k_{i,1} = 5.814 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ ,  $k_{i,2} = 0.075 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ ,  $k_p = 0.131 \text{ L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{min}^{-1}$ , and  $\epsilon = 0.1, \dots, 0.7$ ) by applying the three methods for calculating the intercept  $t_0$  [1]: 1) linear regression of the final points of the  $q(t)$  curve, 2) fitting  $q(t)$  with a hyperbolic branch, and 3) fitting  $q(t)$  with a rational function. The approximate values of  $k_p$  calculated from the final slope and of  $k_{i,2}$  calculated with Eqs. (22) and (23) are listed in Table 2.

We also present the results obtained by processing the data gathered in three experiments of anionic polymerization of styrene with *n*-BuLi, performed at 8.5°C (Exp. 1), 10°C (Exp. 2), and 25°C (Exp. 3). For each set of experimental data, the slope and intercept of the asymptote were determined by using the three methods described in Ref. 1;  $k_p$  was calculated from the slope and  $k_{i,2}$  with Eqs. (22) and (23). The resulting constants are:

For Exp. 1:  $k_p = 0.115 \text{ L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{min}^{-1}$ ,  $k_{i,2} = 0.031 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ ,  
 For Exp. 2:  $k_p = 0.123 \text{ L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{min}^{-1}$ ,  $k_{i,2} = 0.036 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ ,  
 For Exp. 3:  $k_p = 0.647 \text{ L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{min}^{-1}$ ,  $k_{i,2} = 0.16 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ .

The above values are those that lead to the smallest standard deviation ( $q_{II}$  from  $q$ ) from the three sets of constants calculated for each experiment (Fig. 3).

The method of computer fitting the experimental data with Eq. (26) was also tested. We again used the data obtained in the numerical integration of Set (1) with the rate constants  $k_{i,1} = 5.814 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ ,  $k_{i,2} = 0.075 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ , and  $k_p = 0.131 \text{ L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{min}^{-1}$ , and we used the following starting values for the fitting:  $k_{i,2} = 0.15 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$  and  $k_p = 0.2 \text{ L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{min}^{-1}$ . The results were  $k_{i,2} = 0.085 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$  and  $k_p = 0.126 \text{ L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{min}^{-1}$ .

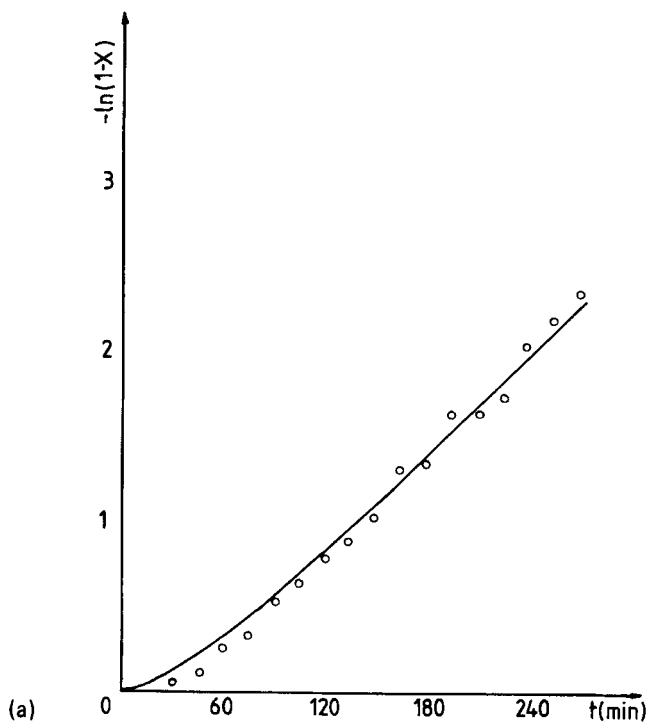
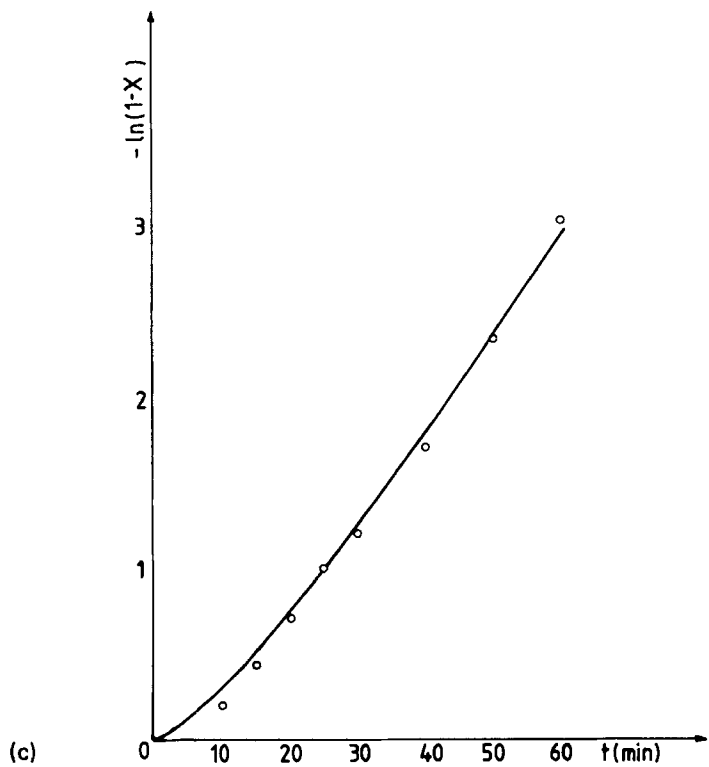
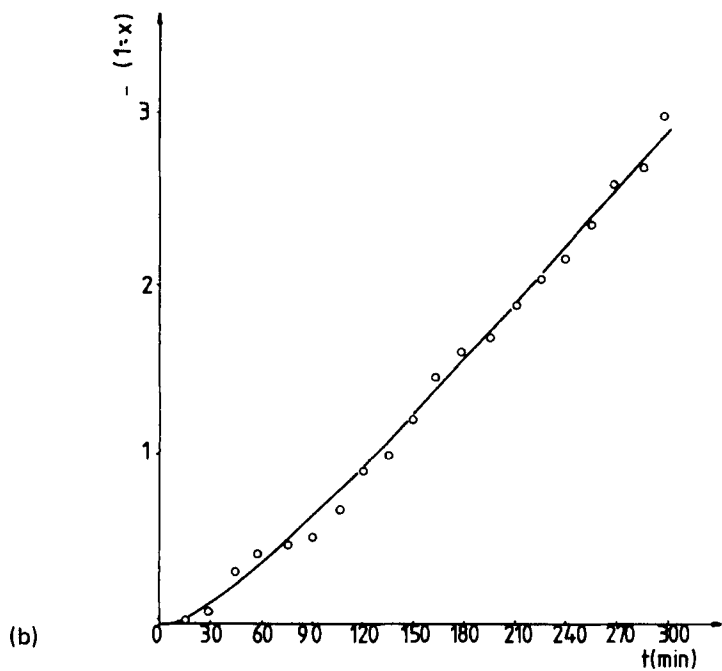


FIG. 3. Plot of the function  $q_{II}$  (—) obtained by processing the data from three anionic polymerizations of styrene: (a) Exp. 1, (b) Exp. 2, (c) Exp. 3. The open circles represent points.



### CONCLUSIONS

For the usual conditions of polymerization (small  $\epsilon$ 's), the obtained approximate analytical solutions of Set (1) are in good agreement with a solution calculated by numerical integration (the second-order approximation being, however, more accurate than the first-order approximation).

Hence, the approximate formulas for  $k_{i,2}$  based upon these solutions yield values of this rate constant which are very close to the true one.

For unusual large  $\epsilon$ 's, when Eqs. (22) and (23) do not provide very good approximations of  $k_{i,2}$ , two procedures may be followed: one consists of selecting  $[I]_0$  and  $[M]_0$  so as to obtain a small  $\epsilon$  and performing another polymerization with these new initial concentrations, while the other one consists in fitting the experimental  $q$  data with the approximate Eq. (26).

### APPENDIX

Set (5) is written in the form

$$\begin{aligned} dp_0(\tau)/d\tau + \epsilon dp_1(\tau)/d\tau + \epsilon^2 dp_2(\tau)/d\tau + \dots = (1 - p_0(\tau)) \exp(-q_0(\tau)) \\ - \epsilon[(1 - p_0(\tau))q_1(\tau) + p_1(\tau)] \exp(-q_0(\tau)) + \dots, dq(\tau)/d\tau \\ + \epsilon dq_1(\tau)/d\tau + \epsilon^2 dq_2(\tau)/d\tau + \dots = \epsilon p_0(\tau)^{1/2} + \epsilon^2 (1/2)p_0(\tau)^{-1/2} p_1(\tau) \\ + \dots \end{aligned} \quad (\text{A.1})$$

By identifying the  $\epsilon^0$  terms in the two equations, it follows that

$$q_0(\tau) = 0$$

$$p_0(\tau) = 1 - \exp(-\tau).$$

Then, by equating the  $\epsilon$  terms in Eq. (A.1)<sub>2</sub>, we obtain  $dq_1(\tau)/d\tau = p_0(\tau)^{1/2}$ , i.e.,

$$q_1(\tau) = \int_0^\tau [1 - \exp(-s)]^{1/2} ds.$$

After integration

$$q_1(\tau) = \tau - 2 \left\{ (1 - \exp(-\tau))^{1/2} - \ln [1 + (1 - \exp(-\tau))^{1/2}] \right\}. \quad (\text{A.2})$$

The  $\epsilon$  terms in Eq. (A.1)<sub>1</sub> lead to

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

from which it follows that

$$p_1(\tau) = -\exp(-\tau) \int_0^\tau q_1(s) ds.$$

The  $\epsilon^2$  terms of Eq. (A.1)<sub>2</sub> are now equated to obtain

$$dq_2(\tau)/d\tau = (1/2)p_0(\tau)^{-1/2}p_1(\tau),$$

and after the substitutions,

$$dq_2(\tau)/d\tau = -(1/2)(1 - \exp(-\tau))^{-1/2} \exp(-\tau) \int_0^\tau q_1(s) ds.$$

By observing that

$$(1/2)(1 - \exp(-\tau))^{-1/2} \exp(-\tau) = d(1 - \exp(-\tau))^{1/2}/d\tau,$$

we may write

$$q_2(\tau) = - \int_0^\tau (d(1 - \exp(-s))^{1/2}/ds) \left[ \int_0^s q_1(u) du \right] ds.$$

It follows that

$$q_2(\tau) = -(1 - \exp(-\tau))^{1/2} \int_0^\tau q_1(s) ds + (1/2)q_1(\tau)^2,$$

and after performing the calculations, the expression for  $q_2$  given by Eq. (10) is obtained.

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