The Quasi-Stationary State Approximation in Polymerization Kinetics

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Synopsis

The errors incurred in free-radical chain addition polymerizations through the use of the popular quasi-stationary state approximation (QSSA) under severe, but fairly common, reaction conditions are examined in detail, and simple, useful criteria for applicability of the QSSA are proposed. The conditions examined are "dead end" polymerization, polymerization with hindered termination and nonisothermal polymerization. It is concluded that the proposed criteria are reasonably accurate and that in most known free-radical polymerizations only hindered termination might possibly lead to appreciable errors through application of the QSSA.

INTRODUCTION

A familiar reaction scheme in chemical kinetics is the sequence

$$\mathrm{I} \xrightarrow{\ k_i\ } \mathrm{P^*} \xrightarrow{\ k_t\ } \mathrm{P} \tag{1}$$

in which desired product P is formed from initial reagent I through intermediate $\mathrm{P^*}$. The rate of formation of product depends upon the concentration of intermediate $[\mathrm{P^*}]$, which must be found by solving its population balance

$$\frac{d[\mathrm{P^*}]}{dt} = R_i - R_t. \tag{2a}$$

R_i and R_t are rate functions for generation and destruction of the intermediate, respectively. We consider in the present study only cases in which

$$R_i = k_i[\mathrm{I}] \tag{2b}$$

and

$$R_t = k_t[\mathrm{P^*}]^\nu \tag{2c}$$

where ν may have a value of either 1 or 2.

In many reactions conforming to scheme 1, $\mathrm{P^*}$ is a so-called *active* intermediate such as a free radical, ion, or catalyst complex. One manifestation

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of an active intermediate is that $[P^*]$ is very small. A concomitant characteristic of reaction sequences involving active intermediates, called chain reactions, is the existence of a quasi-stationary state (QSS) in which

$$R_i \approx R_t. \tag{3}$$

Since eq. (2a) is often difficult or impossible to solve analytically, most kinetic analyses of chain reactions rely for computation of $[P^*]$ upon the so-called quasi-stationary state approximation (QSSA). The QSSA, which is often remarkably accurate, states that $[P^*]$ may be computed from an approximate algebraic expression

$$[P^*] \approx \left[\frac{R_i}{k_t} \right]^{1/\nu} \equiv [P^*]_s. \tag{4}$$

While $d[P^*]/dt$ has been set equal to zero in eq. (2) in order to obtain eq. (4), the QSSA does not assume that $[P^*]$ is constant with time. It merely asserts that the concentration of intermediates in chain reactions, even though they are time dependent, may be closely approximated by a simple relationship such as eq. (4), as long as $d[P^*]/dt$ is small with respect to the remaining terms in eq. (2).

Chain-addition polymerizations take place through active intermediates according to a reaction sequence analogous to eq. (1) in which I is initiator and P is polymer, and their intermediates obey population balance (2). Consider, for example, the polymerization scheme

$$I \xrightarrow{k_d} R^* \qquad \text{initiator decomposition or}$$
$$\text{kinetic chain initiation}$$

$$R^* + m \xrightarrow{k_i'} m_1^* \qquad \text{polymer chain initiation}$$

$$m_x^* + m \xrightarrow{k_P} m_{x+1}^* \quad \text{for } x \geq 1 \tag{5}$$
$$\text{chain propagation}$$

$$\left. \begin{array}{l} R^* \xrightarrow{k_i'} R \\ m_x^* \xrightarrow{k_t} m_x \text{ for } x \geq 1 \end{array} \right\} \text{ chain termination}$$

However, it should be noted that scheme (5), unlike eq. (1), involves two reactants, I and m. It is customary to combine the termination reaction involving primary active intermediates, R^*, with the two initiation steps into a single rate function by introducing an efficiency factor f. The rate functions for termination and polymer chain initiation thus become, respectively, relation (2c) and

$$R_i = \nu f k_d [I] = k_i [m]^n [I] \tag{6}$$

where

$$[P^*] \equiv \sum_{x=1}^{\infty} [m_x^*]. \tag{7}$$

Since f is generally dependent upon monomer concentration $[m]$, fk_d is sometimes[1] replaced with the function $k_1[m]^n$, where n is chosen in such a way as to describe the monomer dependence of f. To simplify matters in the present study, we let $n = 0$ in eq. (6) and $\nu f k_d = const. = k_i$, so that expression (6) reduces to (2b). It is now clear that the sum of all active polymeric intermediates, P^*, as defined in eq. (7), obey eqs. (2).

In the analysis of polymerizations, we are primarily interested in monomer conversion

$$\Phi \equiv \frac{[m]_0 - [m]}{[m]_0} \tag{8}$$

and number-average degree of polymerization

$$\bar{x}_N = \frac{[m]_0 - [m]}{[I]_0 - [I]} \tag{9}$$

where initiator and monomer obey the following rate equations:

$$-\frac{d[I]}{dt} = k_i[I] \tag{10}$$

$$-\frac{d[m]}{dt} \approx k_p[m][P^*]. \tag{11}$$

To determine Φ and $\bar{x}_N$ rigorously, it is necessary to solve eqs. (10) and (11) simultaneously with eq. (2), which contains $[P^*]$. Their approximate values may be obtained via the QSSA by substituting $[P^*]_s$ from eqs. (2b) and (4) into eq. (11). This gives the "classical" result

$$-\frac{d[m]}{dt} = k_P\left[\frac{k_i}{k_t}\right]^{1/\nu}[m][I]^{1/\nu} \tag{12}$$

whose solution is substituted into eqs. (8) and (9).

Numerous contributions have been made concerning the QSSA[2-5] as well as higher-order approximations,[7,8] of the solution of eq. 2 for active intermediate concentration. Only a few are cited in refs. 2–8. Of these, all have confined their analyses to isothermal reactor conditions, and three[2-4] have considered polymerization reactions. In all but one,[4] emphasis was placed on the errors incurred in the computation of $[P^*]$, through the application of approximations, without further consideration of how these errors might affect the subsequent computation of other kinetic variables such as Φ and $\bar{x}_N$.

The following criteria have been proposed for the validity of the QSSA:

$$k_t/k_i \gg 1 \tag{13}$$

when $\nu = 1$[4,6,8] and

$$\sqrt{\frac{k_t[I]_0}{k_i}} \gg 1 \tag{14}$$

when $\nu = 2$.[8]   These inequalities suggest that the QSSA might be violated when k_i increases and/or k_t decreases.   The objective of the present study is to examine in more detail the validity and consequences of the QSSA when applied to chain-addition polymerizations, especially in three specific situations which commonly occur with free-radical ($\nu = 2$) polymerizations on an engineering scale.   These situations, which represent severe reaction conditions, are:

  1.   "Dead end" polymerization,[1,9] where k_i in eq. (10) is large.

  2.   Polymerization with hindered termination as in the "gel effect"[10] and in precipitous polymerizations where k_t is either very small and constant[3] or a rapidly decreasing function of time, $k_t(t)$.[11]

  3.   Nonisothermal reactor conditions[12] where $k_i(t)$ and $k_t(t)$ are both strong functions of time resulting from their Arrhenius temperature dependence $k = A \exp(-E/RT)$ and the time-varying thermal history $T(t)$ which the polymerization experiences.

THEORY

  The criteria ordinarily used to estimate whether or not the QSSA is valid have been that $[P^*]$ and the "relaxation time" required to reach $[P^*]_s$ both be small.[8]   Boudart[6] has rephrased these on the basis of analytical solutions of eqs. (2) and (10) for $[P^*]$ when $\nu = 1$.   One of his criteria is inequality (13), which defines P^* as an *active* intermediate and is equivalent to requiring that its concentration be small.   The other states that the QSSA may only be applied to reaction times which exceed the mean lifetime of the active intermediates and that the latter is equal to the relaxation time of the QSSA.

  Since the mean lifetime of active polymeric chain intermediates in addition polymerizations, λ_p, is easy to estimate from physical considerations, we shall pursue this line of reasoning and require that reaction times t satisfy the inequality

$$t > \lambda_P \tag{15}$$

in order for the QSSA to be applicable.

  We define (see Appendix)

$$\lambda_{P_1} = 1/k_t \tag{16}$$

when $\nu = 1$ and

$$\lambda_{P_2} \equiv 1/\sqrt{k_i k_t [\mathrm{I}]_0} \tag{17}$$

when $\nu = 2$.   Either of these may be substituted into criterion (15), which clearly concerns itself with the range of applicability of the QSSA in reaction time.   However, in order to formulate more practical criteria which relate to the range of conversion of reactants in which the QSSA is applicable, we also define (see Appendix) characteristic times for initiator depletion, λ_i, and monomer conversion, λ_m, as

$$\lambda_i \equiv 1/k_i \tag{18}$$

for both $\nu = 1$ and $\nu = 2$,

$$\lambda_{m_1} \equiv \frac{k_t}{k_P k_i [\mathrm{I}]_0} \tag{19}$$

when $\nu = 1$ and

$$\lambda_{m_2} \equiv \frac{1}{k_P} \sqrt{\frac{k_t}{k_i [\mathrm{I}]_0}} \tag{20}$$

when $\nu = 2$. It is obvious that polymerization will cease when either reactant, viz., I or m, has been used up. We shall refer to the extreme cases in which monomer disappears more rapidly than initiator as "conventional" polymerization and its opposite, following Tobolsky, as "dead end" polymerization, and formulate criteria for their existence in terms of our characteristic times as follows:

conventional polymerization

$$\lambda_i > \lambda_m \tag{21}$$

dead-end polymerization

$$\lambda_m > \lambda_i \tag{22}$$

Thus, it is reasonable to expect the QSSA to be valid in dead-end polymerizations when

$$\lambda_P \ll \lambda_i \tag{23}$$

and in conventional polymerizations when

$$\lambda_P \ll \lambda_m. \tag{24}$$

From inequalities (21) and (22) it is clear that both criteria (23) and (24) are actually satisfied once the relevant one is satisfied.

By substituting appropriate definitions from among (16), (17), (18), (19), and (20) into inequalities (23) and (24), we can formulate QSSA criteria for conventional and dead-end chain polymerizations with $\nu = 1$ or $\nu = 2$. In the present study we shall only be concerned with free-radical intermediates ($\nu = 2$) for which we summarize the criteria for the QSSA as follows:

$$t > \lambda_P = 1/\sqrt{k_i k_t [\mathrm{I}]_0} \tag{I}$$

dead-end
($\alpha < \beta$)

$$\lambda_i/\lambda_P = \sqrt{\frac{k_t [\mathrm{I}]_0}{k_i}} \equiv \alpha \gg 1 \tag{II}$$

conventional $\lambda_m/\lambda_P = k_t/k_P \equiv \beta \gg 1$ (III)
($\alpha > \beta$)

However, we should note that criterion (23), together with definition (16) does agree with that of Boudart[6] for the case $\nu = 1$, and criterion (II) with that of Bowen et al.[8] for the case $\nu = 2$. The latter authors, as well as Ray,[4] with $[m]_0$ replacing $[I]_0$, have made use of (II) but not of (III), which appears to be of considerable value in many free-radical polymerizations since, as we shall learn, (II) is virtually impossible to violate even with dead-end initiation.

In summary, then, we propose that the QSSA is valid over virtually the entire practical range of interest in a chain-addition polymerization from start to finish only when both criteria (II) and (III) are satisfied. If either one is violated, then the QSSA does not apply. For instance, if (II) is satisfied but not (III), then the QSSA may not be valid over the entire range of monomer conversion. Similarly, if (III) is satisfied and not (II), then initiator will be used up before all of the monomer has been converted to polymer, and a deviation from the QSSA may occur before polymerization ceases. We should also note from (I), (II), and (III) that, whereas the effects of a small value of k_t all point in the same direction, viz., toward longer relaxation times and smaller ranges of applicability of the QSSA, a large value of k_t will actually shorten the relaxation time while still reducing the range of the QSSA relative to initiator depletion. Moreover, the presence of $[I]_0$ in (I) and (II) should not be taken too seriously since a rapid rate of initiation will produce a large deviation in $[I]$ from its initial value and cause these criteria to become less well satisfied as polymerization proceeds. For instance, 99% depletion in initiator will increase λ_P and reduce α by one order of magnitude from their values based upon $[I]_0$.

These criteria are difficult to apply with any reasonable degree of accuracy to situations in which k_i and k_t are strong functions of time. Certainly the behavior of nonisothermal polymerizations will be determined by the relative magnitudes of the activation energies for initiation, propagation, and termination, E_i, E_P and E_t, respectively. It appears that the relaxation time of the QSSA at high temperatures will be shorter than that at low temperatures. However, if $E_i > E_t$, as is often the case, it is probable that the range of the QSSA with respect to initiator depletion will decrease with increasing temperature.

COMPUTATIONS

Dead-End Polymerization

Equations (2a), (4), (10), and (11) are written in dimensionless form by reducing concentrations and time to dimensionless variables with $[I]_0$ and λ_t, respectively. Thus,

$$\frac{dP}{d\tau} = I - \alpha^2 P^2 \qquad P_0 = 0 \tag{25}$$

$$P_s = I^{1/2}/\alpha \tag{26}$$

$$-\frac{d\mathrm{I}}{d\tau} = \mathrm{I} \qquad \mathrm{I}_0 = 1 \qquad\qquad (27)$$

$$-\frac{d\mathrm{m}}{d\tau} = \frac{\alpha^2}{\beta}\,\mathrm{mP} \qquad \mathrm{m}_0 = \frac{[\mathrm{m}]_0}{[\mathrm{I}]_0} \qquad\qquad (28)$$

Following Boudart,[6] the error between the true and QSS values for [P*] is defined as

$$\epsilon \equiv 1 - \mathrm{P}/\mathrm{P}_s. \qquad\qquad (29)$$

The QSS value for monomer concentration is obtained from eq. (28) after replacing P with P_s,

$$\mathrm{m}_s = \mathrm{m}_0 \exp\left\{\frac{2\alpha}{\beta}\left[\exp\left(-\frac{\tau}{2}\right) - 1\right]\right\} \qquad\qquad (30)$$

and subsequently used in eq. (9) to calculate the QSS value of $\bar{x}_N$.

When the QSSA is not invoked, it is necessary to solve coupled eqs. (25), (27), and (28) simultaneously.

Polymerization with Hindered Termination

We use the following simple function to simulate the dependence of k_t on Φ:

$$k_t = k_{t_0} \exp[-\beta\Phi] \qquad\qquad (31)$$

where k_{t_0} and B are adjustable constants. With the aid of expression (31), eqs. 25, 26, and 28 are modified to

$$\frac{d\mathrm{P}}{d\tau} = \mathrm{I} - \alpha_0^2\mathrm{P}^2 \exp[-B\Phi] \qquad\qquad (32)$$

$$\mathrm{P}_s = [\mathrm{I}\exp(B\Phi)]^{1/2}/\alpha_0 \qquad\qquad (33)$$

$$-\frac{d\mathrm{m}}{d\tau} = \frac{\alpha_0^2}{\beta}\,\mathrm{mP}\,\exp\left\{-B\left(1 - \frac{\mathrm{m}}{\mathrm{m}_0}\right)\right\} \qquad\qquad (34)$$

and m_s is obtained by solving

$$-\frac{d\mathrm{m}_s}{d\tau} = \frac{\alpha_0}{\beta}\,\mathrm{m}_s\left\{1\,\exp\left[B\left(1 - \frac{\mathrm{m}_s}{\mathrm{m}_0}\right)\right]\right\}^{1/2}. \qquad\qquad (35)$$

When the QSSA is not invoked, eqs. (27), (32), and (34) must be solved simultaneously.

Nonisothermal Polymerizations

For polymerizations with a nonisothermal temperature schedule, $T(t)$, it is necessary to solve the following equations simultaneously:

$$\frac{d\mathrm{P}}{dt} = A_i \exp[-E_i/RT(t)]\mathrm{I} - A_t[\mathrm{I}]_0 \exp[-E_t/RT(t)]\mathrm{P}^2 \qquad (36)$$

$$P_s = \left\{ \frac{A_i \exp[-(E_i - E_t)/RT(t)]\mathrm{I}}{A_t[\mathrm{I}]_0} \right\}^{1/2} \tag{37}$$

$$-\frac{d\mathrm{I}}{dt} = A_i \exp[-E_i/RT(t)]\mathrm{I} \tag{38}$$

$$-\frac{d\mathrm{m}}{dt} = A_p[\mathrm{I}]_0 \exp[-E_P/RT(t)]\mathrm{mP} \tag{39}$$

which are again versions of (2a), (4), (10), and (11), only with their temperature dependence exposed.

The QSS value for m is given by

$$\ln \frac{\mathrm{m}_s}{\mathrm{m}_0} = -A_P[\mathrm{I}]_0 \left\{ \frac{A_i}{A_t[\mathrm{I}]_0} \right\}^{1/2} \int_0^t \exp[-E_A/RT(t)]\mathrm{I}^{1/2}\, dt \tag{40}$$

where $E_A \equiv E_P + (E_i - E_t)/2 =$ apparent activation energy from eq. (12).

The temperature schedule used in this study was a linear one,

$$T(t) = T_0 + aT$$

with two variations, or modes. They were:

Mode A

$$T_0 = 400°\mathrm{K}$$

first: $a = 0.5°\mathrm{K/sec}$ for $400 \leq T \leq 420°\mathrm{K}$

then: $a = -0.5°\mathrm{K/sec}$ for $420 \geq T > 373°\mathrm{K}$

Mode B

$$T_0 = 402°\mathrm{K}$$

first: $a = 0.7°\mathrm{K/sec}$ for $402°\mathrm{K} \leq T < 470°\mathrm{K}$

then: $a = 5°\mathrm{K/sec}$ for $470°\mathrm{K} \leq T < 700°\mathrm{K}$

Two sets of values were also used for the Arrhenius pair A_i, E_i. They were 10^{15} sec^{-1}, 32 kcal, and 1 sec^{-1}, 7 kcal. The first pair is typical for free-radical polymerizations, and the second pair was chosen for convenience, but in such a way as to give the same value for k_i as the first at room temperature.

Other kinetic parameters used in the computations, which are also typical in value, are:

$$[\mathrm{m}]_0 = 1 \text{ mole/l.}$$

$$[\mathrm{I}]_0 = 10^{-3} \text{ mole/l.}$$

$$A_t = 1.25 \times 10^9 \text{ l./mole sec}$$

$$A_P = 10^7 \text{ l./mole sec}$$

$$E_t = 1.68 \text{ kcal/mole}$$

$$E_P = 7 \text{ kcal/mole}$$

All numerical calculations were performed on a PDP-10 digital computer. The Runge-Kutta fourth-order integration method was used to solve the simultaneous differential equations. Integration step size as small as 10^{-6} in dimensionless time (τ) was necessary in some computations to insure accuracy of results.

RESULTS AND CONCLUSIONS

It is well known that for chain polymerizations via free-radical intermediates, the following represent typical kinetic parameters:

$$k_i \sim 10^{-5} \text{ l./mole sec}$$

$$k_P \sim 10^4 \text{ l./mole sec}$$

$$k_t \sim 10^8 \text{ l./mole sec}$$

$$\lambda_P \sim 10^{-1} \text{ to } 10 \text{ sec}$$

In carrying out the numerical computations for Figures 1–6, we have violated first α by using large values for k_i (Figs. 1 and 2), then β by using small values for k_t (Figs. 3 and 4), and, finally, both α and β (Figs. 5 and 6), while maintaining values for k_P and λ_P as reasonable as possible in all cases. The errors in $[P^*]$ and $\bar{x}_N$ resulting from the use of the QSSA, which were expected by virtue of criteria (II) and (III), are clearly shown. We shall assign to $[I]_0$ a value of 10^{-3} mole/l. in all subsequent comparisons.
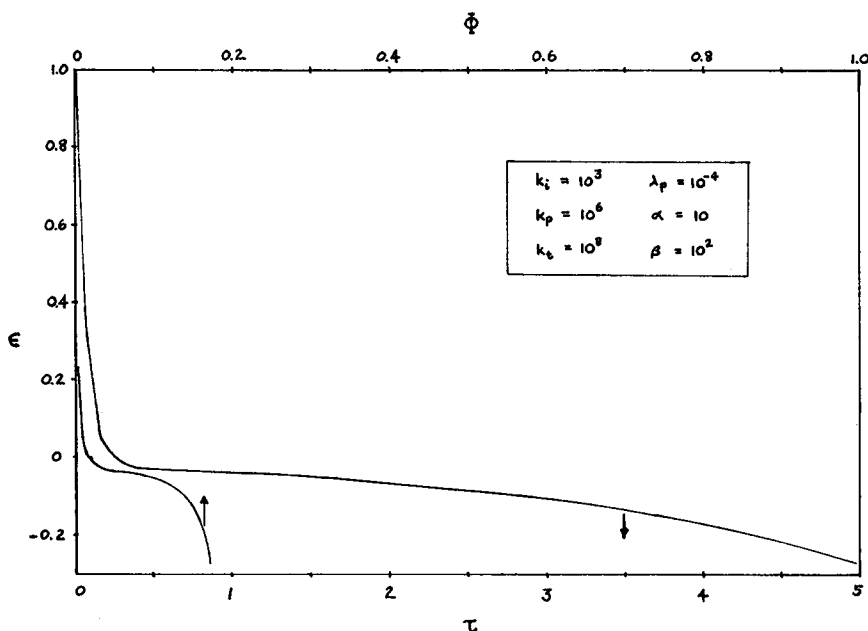
Fig. 1. Plot of ϵ vs. τ and Φ for $\alpha = 10$ and $\beta = 10^2$.

In order to violate criterion (II), values for k_i as large as 10^3 were used, which further necessitated the use (Figs. 1 and 2) of exceptionally large values for k_P in order to achieve any discernible monomer conversion at the time of total initiator depletion.   A by-product of this was the unusually
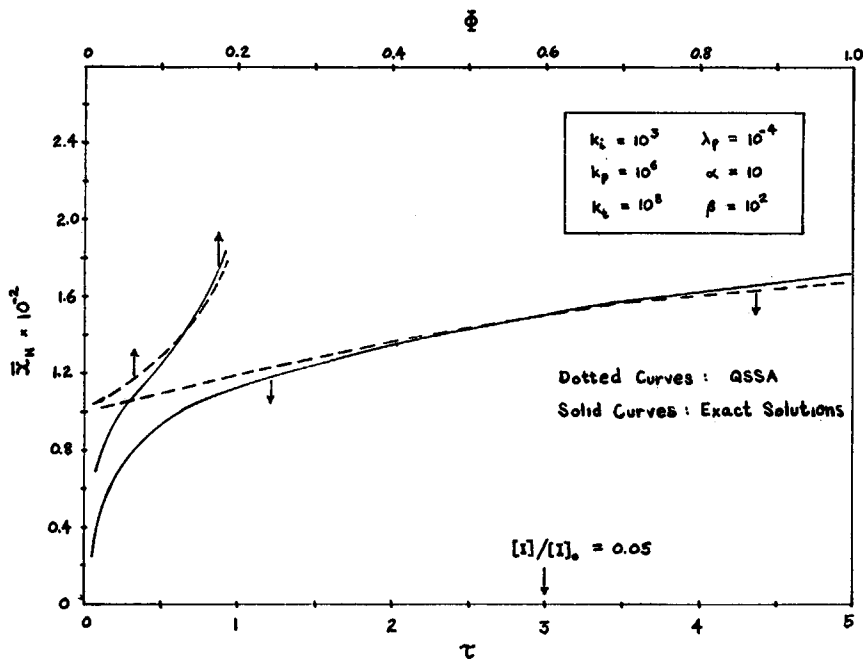
Fig. 2. Plot of $\bar{x}_N$ vs. τ and Φ for $\alpha = 10$ and $\beta = 10^2$.
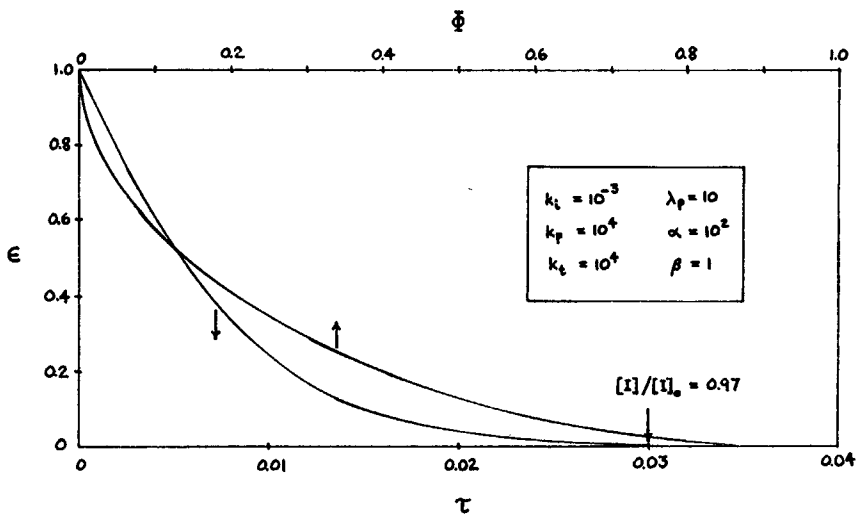
Fig. 3. Plot of ϵ vs. τ and Φ, for $\alpha = 10^2$ and $\beta = 1$.
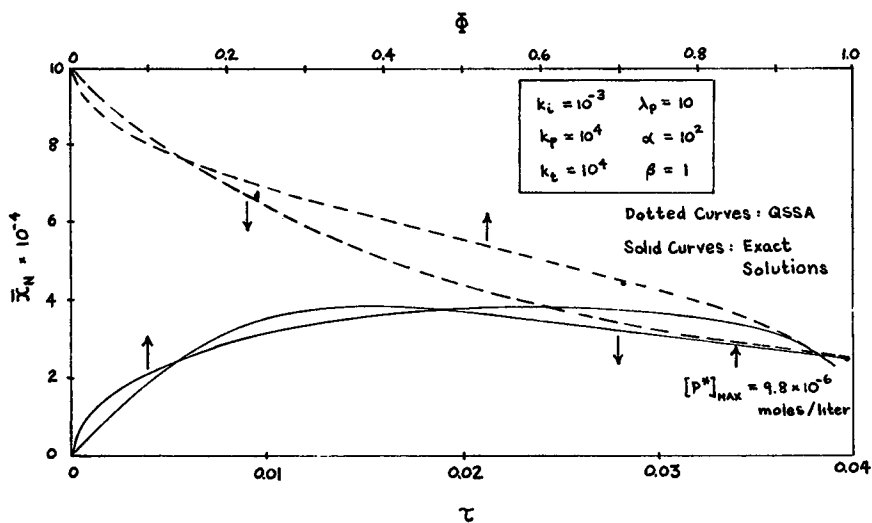
Fig. 4. Plot of $\bar{x}_N$ vs. τ and Φ for $\alpha = 10^2$ and $\beta = 1$.
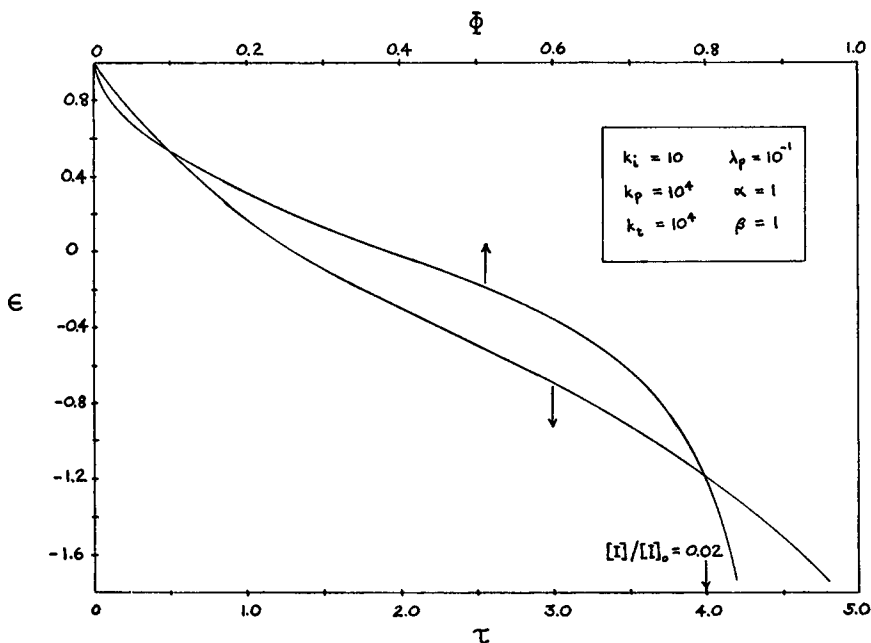
Fig. 5. Plot of ϵ vs. τ and Φ for $\alpha = 1$ and $\beta = 1$.

small value for λ_P which resulted.   The kinetic constants used in Figures 3 and 4 were more reasonable since values for k_i of 10^{-3} (ref. 9) and for k_t as low as 10^4 (refs. 3,13) have previously been reported.   Moreover, even with such small values for k_t, [P*] did not attain a value far in excess of 10^{-5} mole/l., which is probably acceptable.
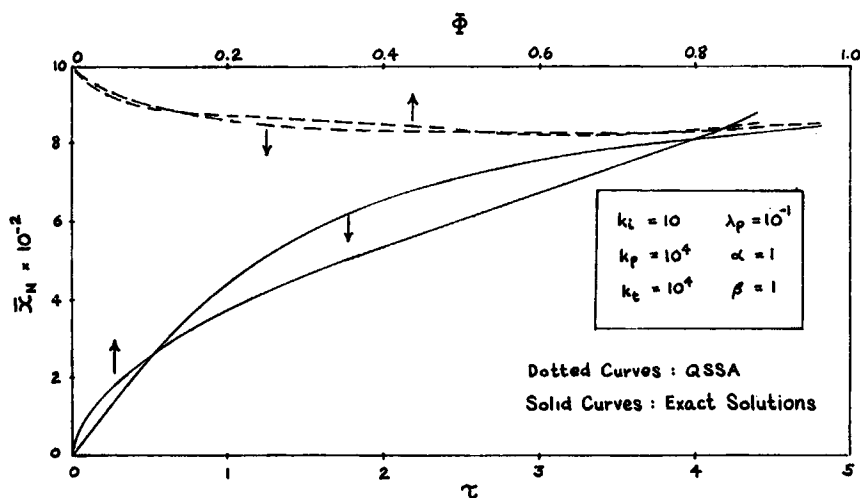
Fig. 6. Plot of $\bar{x}_N$ vs. τ and Φ for $\alpha = 1$ and $\beta = 1$.
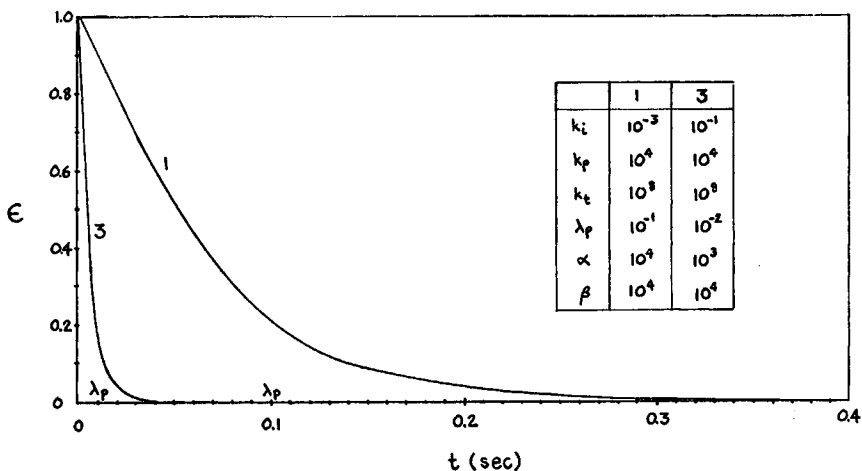
Fig. 7. Relaxation of the QSS error with time.

Figures 7–9 represent more realistically than previous figures the phenomenon called "dead end" polymerization (large k_i) which has been observed for values of $k_i \sim 10^{-3}$ and $k_P \sim 10^8$ (ref. 9). Relaxation to the QSSA is seen in Figure 7 to occur at shorter times, as predicted by criterion (I), the larger is the value of k_t. Notwithstanding this, the range of applicability of the QSSA decreases, as shown in Figure 8 and predicted by criterion (II). We should point out, however, that neither criterion (II) nor (III) is actually violated in dead-end polymerization so that the QSSA actually applies. This is verified by its negligible effect on accuracy in our predictions of $\bar{x}_N$ with monomer conversion in Figure 9. The abrupt deviations from zero error in Figure 8 are due to the total depletion of
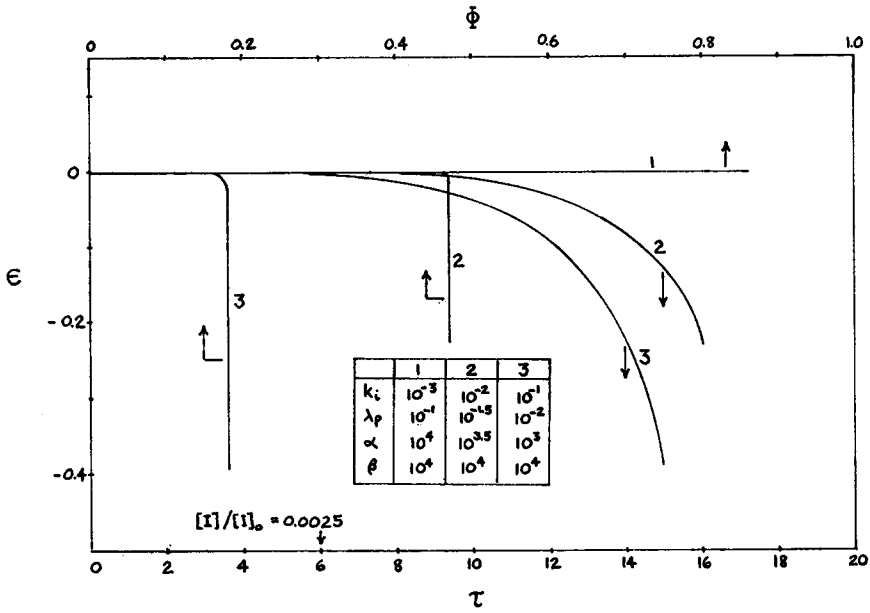
Fig. 8. Plot of ϵ vs. τ and Φ for "dead-end" polymerization.
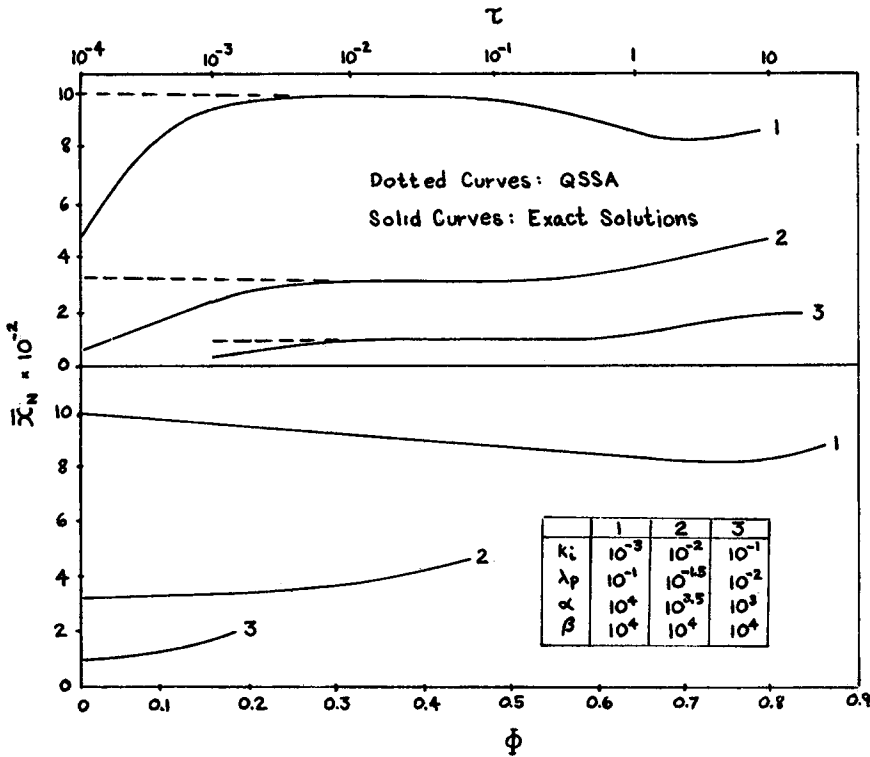
Fig. 9. Plot of $\bar{x}_N$ vs. τ and Φ for "dead-end" polymerization.
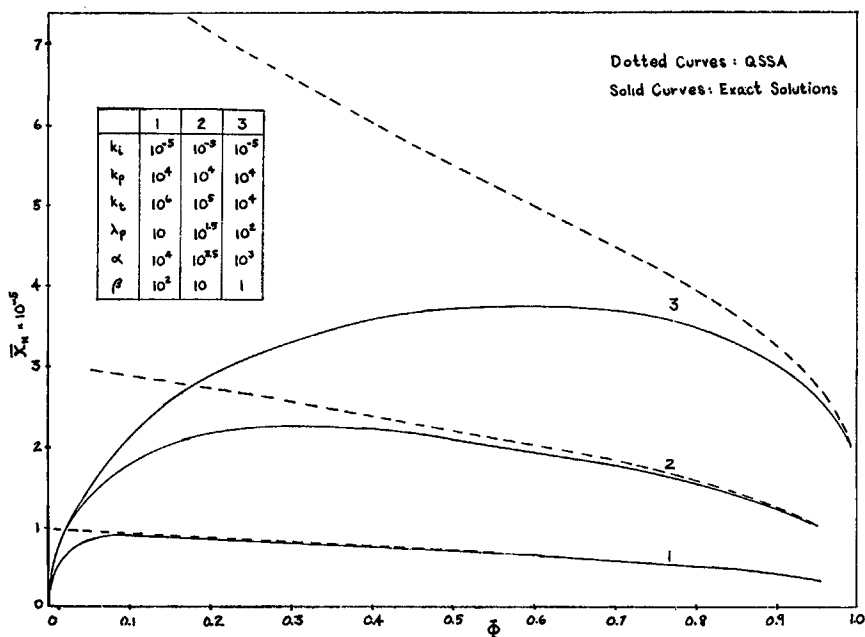
Fig. 10. Plot of $\bar{x}_N$ vs. Φ for hindered termination with low constant k_t.
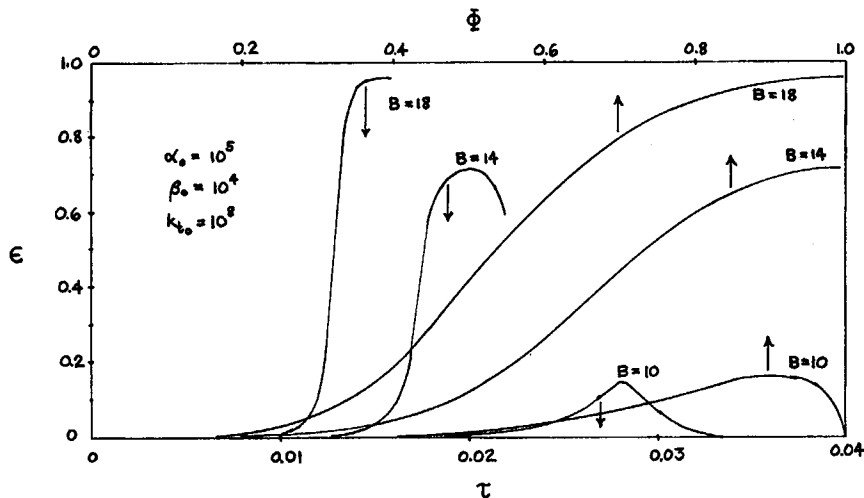
Fig. 11. Plot of ϵ vs. τ and Φ for hindered termination with $k_t = k_{t_0} \exp(-\beta\Phi)$.

initiator at the corresponding monomer conversions, and the large errors in $\bar{x}_N$ in Figure 9 are artifacts created by plotting the logarithm of time. They represent amplifications of the relaxation process and would not be visible at all if linear time were used instead. In order to violate criterion (II), it is necessary to use unreasonably large values of k_t. Ray,[4] for instance, concluded in effect that the QSSA was not valid for values of the kinetic constants equivalent to $k_i \sim 10^2$, $k_P \sim 10^3$, and $k_t \sim 10^8$.

The effect of hindered termination on predictions of $\bar{x}_N$ via the QSSA is shown in Figure 10, whose curves were computed using constant but low values for k_t. It is seen that significant errors are possible over a major portion of the range of monomer conversion as correctly predicted by
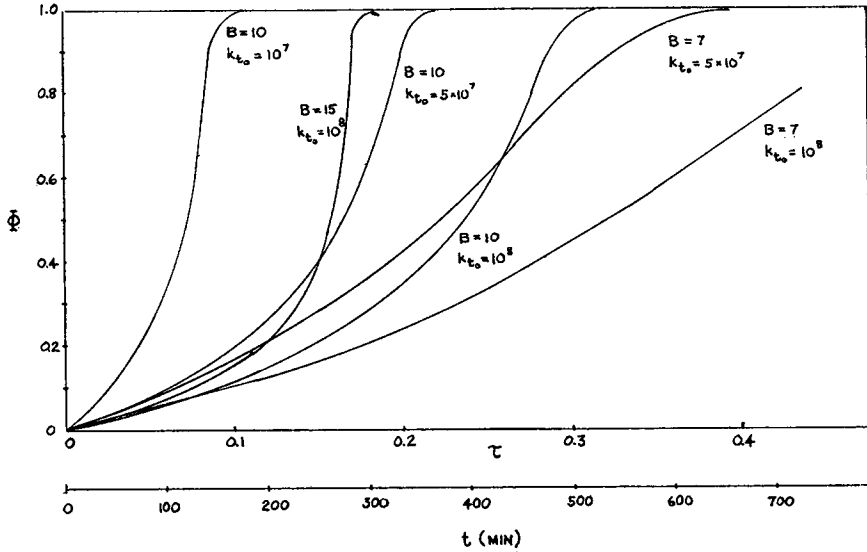
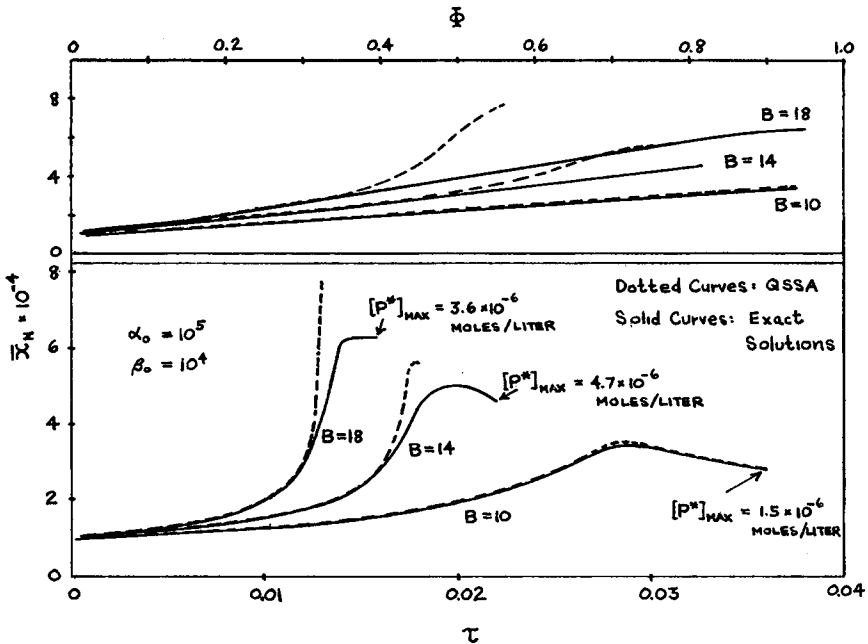Fig. 12. Simulation of diffusion-controlled termination with $k_t = k_{t_0} \exp(-\beta\Phi)$.

Fig. 13. Plot of $\bar{x}_N$ vs. τ and Φ for hindered termination with $k_t = k_{t_0} \exp(-\beta\Phi)$.
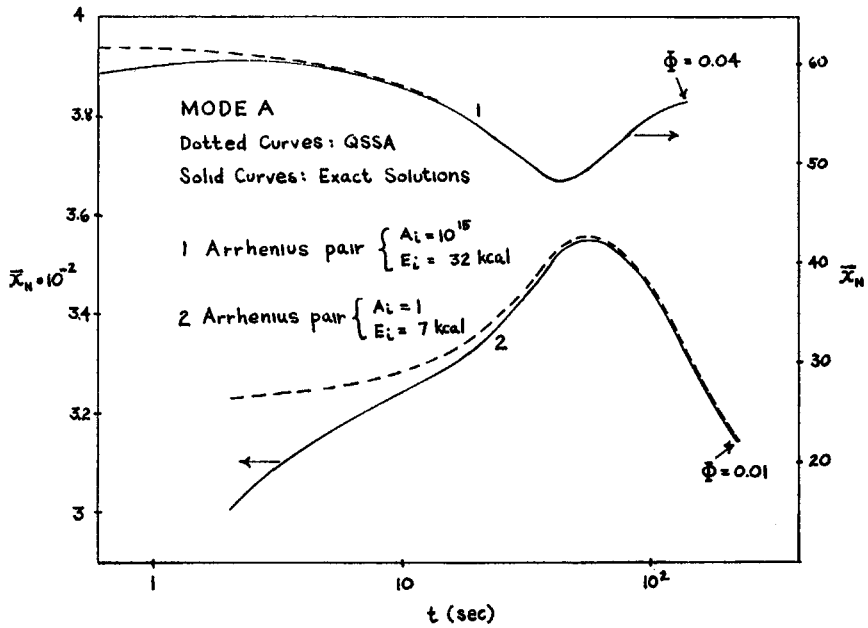
Fig. 14. Plot of $\bar{x}_N$ vs. t for nonisothermal polymerization (mode A).
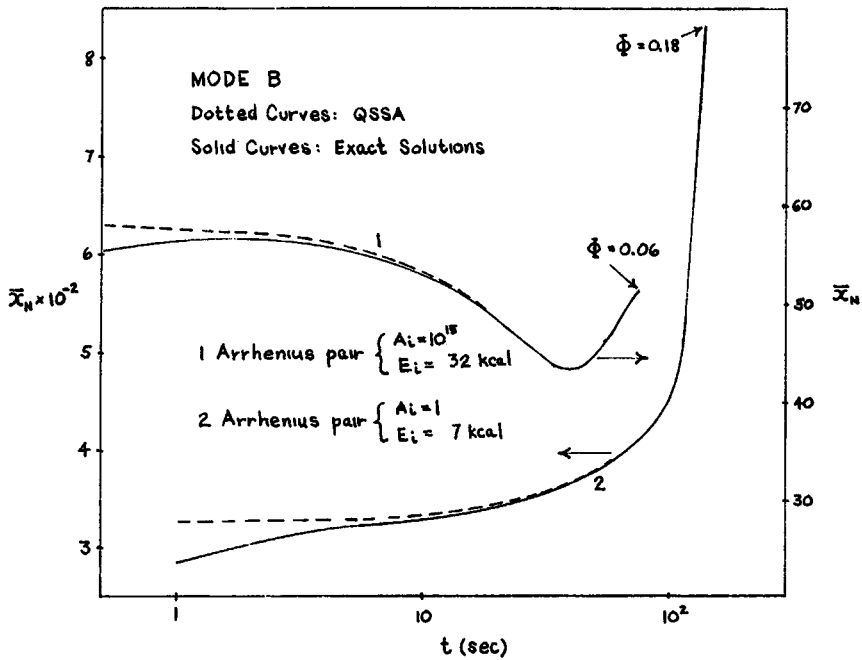
Fig. 15. Plot of $\bar{x}_N$ vs. t for nonisothermal polymerization (mode B).

criterion (III). A similar approach has been used to explain the auto-accelerating rate observed in vinyl chloride polymerizations.[3]

An alternate model for hindered termination in poly(vinyl chloride) formation utilizes a function for k_t which decreases with time[11,14] to simulate the onset of diffusion-controlled termination. We have used a simple exponential function for this purpose, expression (31), with adjustable parameters k_{t_0} and B. This function has been found to be suitable for fitting experimental rate curves in precipitous polymerizations which exhibit autoacceleration.[15] The results are shown in Figures 11–13 for various values of B and with β based on k_{t_0}. If we insist on 10^{-4} as an acceptable upper limit for [P*] up to very high monomer conversions, then B must be assigned a value between 10 and 14 when $k_{t_0} = 10^8$. Significant errors in $\bar{x}_N$ due to the QSSA do not appear until B approaches a value of 14, and then only a fairly high conversions.

Figures 14 and 15 show the effect of the QSSA on predictions of $\bar{x}_N$ for two different temperature schedules, mode A and mode B, and two different Arrhenius pairs, A_t and E_t, for k_t. While 10^{15} and 32 are reasonable values for the preexponential constant and activation energy, respectively, they cause a rapid initiation rate and thus do not permit high conversions to be attained. Another manifestation of rapid initiation is a minimum in $\bar{x}_N$ versus time (curves 1). The other Arrhenius pair, which contains an exceptionally small activation energy, 7, was used in order to achieve higher monomer conversions by reducing the initiation rate. It also causes $\bar{x}_N$ to increase in time (curves 2). The temperature policies were chosen so as to be as severe as possible and to simulate axial temperature profiles predicted for chain polymerizations in tubular reactors[12] under nonrunaway (mode A) and runaway (mode B) conditions.

Deviations in $\bar{x}_N$ from true values, accrued through the use of the QSSA, are seen to be surprisingly small, even when observed in time rather than as a function of Φ. Moreover, relaxation times for the QSSA are actually shorter at high temperatures than at low temperatures, which is predictable from criterion (I), at least qualitatively, since $E_i > E_t$. In conclusion, then, we have shown that the use of the QSSA in chain-addition polymerizations may lead to errors when termination is severely hindered,[3] but appears to be quite justified under other conditions of practical interest; these are dead-end polymerization and even polymerization with rapid changes in temperature.

Appendix

We define λ_t, λ_m, and λ_P in the following equations:

$$R_t \lambda_i = [\text{I}]_0 \tag{A-1}$$

$$R_P \lambda_m = [\text{m}]_0 \tag{A-2}$$

$$R_t \lambda_P = [\text{P*}] \tag{A-3}$$

where R_i is taken as

$$R_i \sim k_t [\text{I}]_0 \tag{A-4}$$

and R_P, the rate of polymerization or monomer conversion, as

$$R_P \sim k_P[m]_0[P^*].$$ (A-5)

If the QSSA is valid, then

$$R_t \sim k_t[P^*]^\nu$$ (A-6)

and $[P^*]$ is approximately given by

$$[P^*] = \left[\frac{k_i[I]_0}{k_t}\right]^{1/\nu}.$$ (A-7)

Expressions (A-4), (A-5), and (A-7), when substituted into definitions (A-1) to (A-3), form the bases for definitions (16)–(20) and subsequently for our criteria, which are thus seen to be at least necessary conditions for the QSSA. It is reassuring, however, that the exact solutions of eqs. (2) with constant $[I] = [I]_0$ for $\nu = 1$,

$$[P^*] = \frac{k_i[I]_0}{k_t}[1 - \exp(-k_t t)]$$ (A-8)

and for $\nu = 2$,

$$[P^*] = \left[\frac{k_i[I]_0}{k_t}\right]^{1/2} \tanh [k_i k_t [I]_0]^{1/2}t$$ (A-9)

would lead us quite naturally to definitions (16) and (17), respectively. Moreover, our criterion for dead-end polymerization, inequality (22), becomes, after substitution of definitions (18) and (20),

$$\frac{1}{k_P}\left[\frac{k_i k_t}{[I]_0}\right]^{1/2} > 1.$$ (A-10)

Finally, criteria for the QSSA may be interpreted and generalized in terms of the population balance for intermediates, eq. (2). First, reduce the concentrations in eq. (2) to their dimensionless forms by dividing by either $[m]_0$ or $[I]_0$. The choice is arbitrary. Second, reduce time to its dimensionless form by dividing by either λ_m or λ_t, whichever is smaller in value. This leads to the dimensionless differential equation, e.g.,

$$\frac{\lambda_P}{\lambda}\frac{dP}{d\tau} = \alpha^{-1}I - \alpha^{\nu-1}P^\nu$$ (A-11)

where the concentrations have been reduced with $[I]$, and where

$$\tau \equiv t/\lambda = \begin{cases} t/\lambda_m \text{ for conventional polymerization} \\ t/\lambda_t \text{ for dead-end polymerization} \end{cases}$$

From (A-11), the QSSA

$$P = \frac{I^{1/\nu}}{\alpha}$$ (A-12)

is valid when

$$\frac{\lambda_P}{\lambda} \ll 1.$$ (A-13)

It is clear that eq. (A-12) reduces to (4) when $\nu = 2$ and that inequality (A-13) reduces to criteria (II) and (III).

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