

Forced Oscillations in Continuous Flow Stirred Tank Reactors with Nonlinear Step Growth Polymerization

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Synopsis

The self-step growth polymerization of RA_f monomers in homogeneous, continuous flow stirred tank reactors (HCSTRs) is simulated under conditions of periodic feed concentration (with frequency ω and amplitude a). By having periodic operation, the polydispersity index of the polymer is found to increase by about 35% over the values at steady state. Periodic operation of HCSTRs is found to lead to gelation only for certain values of the frequency and the dimensionless residence time τ^* . Gelling envelopes have been obtained to give conditions under which HCSTRs should be operated. These envelopes can be described in terms of two critical dimensionless residence times, $\tau_{c,1}^*$ and $\tau_{c,2}^*$ such that nongelling operation is always ensured when $\tau^* < \tau_{c,1}^*$. For $\tau^* > \tau_{c,2}^*$, periodic operation always leads to gelation, and HCSTRs cannot be used. For $\tau_{c,1}^* < \tau^* < \tau_{c,2}^*$, the gelling behavior is found to depend on the functionality f , amplitude a , and the dimensionless residence time τ^* .

INTRODUCTION

It has generally been shown that nonsteady state operation of continuous reactors gives an improved performance compared to operation at steady state.¹⁻⁶ A convenient way by which a given reactor is operated at unsteady state is to vary the feed concentration or the reaction temperature sinusoidally with time. This technique adds one more tool to the repertoire of the polymer engineer to design a reactor-producing polymer of a specified molecular weight distribution.

In a recent review, Meira³ has pointed out that even though several studies, including patents,⁷ have been reported on the periodic operation of chain-growth polymerization reactors, only two^{1,8} have addressed themselves to linear step growth polymerization. Neither of these, however, have considered the effect of forced oscillations in the feed concentration on the performance of the reactor when nonlinear step growth polymerization is taking place. It is well known that several polymers, including crosslinked elastomers, are now produced in continuous flow stirred tank reactors (CSTRs), because of their excellent heat transfer characteristics and other operational advantages. A study of forced oscillations in CSTRs carrying out nonlinear polymerization, therefore, would have considerable industrial importance, since it has been shown^{9,10} that severe limitations are placed

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(because of gelation) on the conversions that can be achieved in such reactors, and any increase in the conversion by the use of forced oscillations will be extremely useful. In this paper, step growth polymerization of RA_f -type multifunctional monomers (where a functional group A reacts with another A group) in isothermal, homogeneous continuous flow stirred tank reactors (HCSTRs, with perfect micromixing) is studied, with the concentration of the monomer in the feed stream varied sinusoidally. This study can easily be modified to account for bang-bang cycling of the feed concentration, imperfect micromixing of the reactor fluid elements, or the effect of nonisothermal operation, using concepts used for other systems,⁸ to reveal information on polymerization reactors with RA_f feed concentrations varied periodically, which may be even more fascinating than those encountered in nonpolymerizing systems.¹⁰

FORMULATION

Mass balance equations for RA_f polymerization in the HCSTR shown in Figure 1 can easily be written as¹¹

$$\frac{d[P_1]}{dt} = \frac{[P_1]_0(t) - [P_1]}{\bar{\theta}} - k \frac{f}{2} [P_1] \sum_{m=1}^{\infty} (mf + 2 - 2m)[P_m] \quad (1a)$$

$$\frac{d[P_n]}{dt} = \frac{-[P_n]}{\bar{\theta}} + \frac{k}{2} \sum_{m=1}^{n-1} (mf + 2 - 2m)\{(n - m)f + 2 - \quad (1b)$$

$$2(n - m)\} \frac{[P_m][P_{n-m}]}{2} - k(nf + 2 - 2n)[P_n] \sum_{m=1}^{\infty} (mf + 2 - 2m) \frac{[P_m]}{2},$$

$$n = 2, 3, \dots$$

where k is the functional group reactivity, $\bar{\theta}$ is the mean residence time ($= V/Q$), t is the time, and $[P_n]$ represents the molar concentration of the n -mer P_n (having $nf - 2n + 2$ unreacted A groups) at time t , both inside the reactor as well as in the output stream (due to the well mixed condition). In eq. (1), $[P_1]_0(t)$ is the molar concentration of the monomer in the feed and is assumed to vary sinusoidally as

$$[P_1]_0(t) = \overline{[P_1]_0} \{1 + a \sin(\omega t)\} \quad (2)$$

where $\overline{[P_1]_0}$ is the time-average value of $[P_1]_0(t)$ given by

$$\overline{[P_1]_0} = \frac{\omega}{2\pi} \int_t^{t+2\pi/\omega} \{[P_1]_0(t)\} dt \quad (3)$$

The concentrations $[P_n]$ are also functions of time, but their dependence on t is not explicitly written in eq. (1) as for $[P_1]_0(t)$. In writing eq. (1), it is assumed that the density is unchanged by reaction, the reactions are irreversible, and that no cyclization takes place.

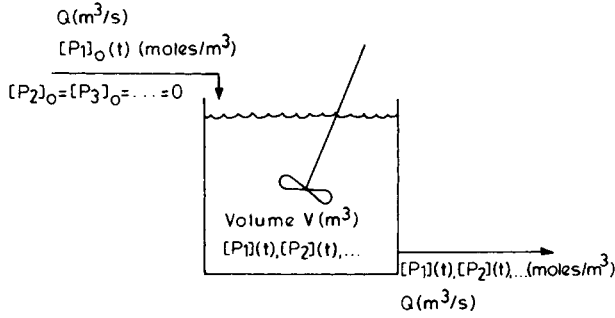


Fig. 1. An HCSTR with constant volume and with constant volumetric inflow and outflow rates. No oligomer except P_1 (and diluent) is present in the feed.

It is interesting to note that the equations characterizing periodic operation of HCSTRs with *random polymer crosslinking* (by reacting together side groups on long polymer chains, or through unsaturation in the chain backbone) are quite similar^{9,12,13} to those given in eq. (1), and are given by

$$\frac{d[P_1]}{dt} = \frac{[P_1]_0(t) - [P_1]}{\theta} - \frac{k}{2}(f - 2)^2 [P_1] \sum_{m=1}^{\infty} m [P_m] \tag{4a}$$

$$\frac{d[P_n]}{dt} = \frac{-[P_n]}{\theta} \tag{4b}$$

$$+ \frac{k}{4}(f - 2)^2 \sum_{m=1}^{n-1} m(n - m) [P_m][P_{n-m}]$$

$$- \frac{k(f - 2)^2}{2} n [P_n] \sum_{m=1}^{\infty} m [P_m];$$

$$n = 2, 3, \dots$$

It can easily be seen that eq. (1) reduces to eq. (4) as $f \rightarrow \infty$ or as molecular weights become large. Thus, periodic operation of HCSTRs with either *polymerization* of low molecular weight RA_f monomers (with f small) or *crosslinking* of high molecular weight RA_f monomers (with f large) can be studied within the same framework.

Equation (1) can be multiplied by n^k ($k = 0, 1, 2, \dots$) and summed up over all values of n appropriately, to give equations for the moments of the chain length distribution

$$\lambda_k \equiv \sum_{n=1}^{\infty} n^k [P_n] \tag{5}$$

These equations can then be made dimensionless and written in terms of the following variables:

$$\tau = t/\bar{\theta} \quad (6a)$$

$$\tau^* = \frac{k}{2}(f-2)^2 \overline{[P_1]_0} \bar{\theta} \quad (6b)$$

$$x_1 = [P_1]/\overline{[P_1]_0} \quad (6c)$$

$$x_{1,0}(\tau) = [P_1]_0(t)/\overline{[P_1]_0} = 1 + a \sin(\omega\bar{\theta}\tau) \quad (6c)$$

$$x_2 = [P]/\overline{[P_1]_0} = \lambda_0/\overline{[P_1]_0} \quad (6d)$$

$$x_3 = (\lambda_2 - \lambda_1)/\overline{[P_1]_0} \quad (6e)$$

$$x_4 = \lambda_1/\overline{[P_1]_0} \quad (6f)$$

The final equations for polymerization of RA_f monomer are obtained as

$$\frac{dx_1}{d\tau} = x_{1,0}(\tau) - x_1 - \frac{f}{f-2}\tau^*x_1x_4 - \frac{2f}{(f-2)^2}\tau^*x_1x_2 \quad (7a)$$

$$\frac{dx_2}{d\tau} = x_{1,0}(\tau) - x_2 - \frac{\tau^*}{2}x_4^2 - \frac{2\tau^*}{(f-2)^2}x_2^2 - \frac{2\tau^*}{f-2}x_2x_4 \quad (7b)$$

$$\frac{dx_3}{d\tau} = 0 - x_3 + \tau^*(x_3 + x_4)^2 + \frac{4}{f-2}\tau^*x_4(x_3 + x_4) + \frac{4\tau^*}{(f-2)^2}x_4^2 \quad (7c)$$

$$\frac{dx_4}{d\tau} = x_{1,0}(\tau) - x_4 \quad (7d)$$

$$x_{1,0}(\tau) = 1 + a \sin(\omega\bar{\theta}\tau) \quad (7e)$$

These may easily be solved with appropriate initial conditions, using the fourth-order Runge-Kutta algorithm. Corresponding equations for cross-linking can also be written. The time-average values of x_i are given by

$$\bar{x}_i = \frac{\omega\bar{\theta}}{2\pi} \int_{\tau}^{\tau+2\pi/\omega\bar{\theta}} x_i(\tau) d\tau \quad (8)$$

with τ usually taken large enough to ensure steady, periodic behavior.

Equations (7b-d) reduce to the earlier equations¹¹ for the case when non-periodic, steady-state feed concentrations are used. Also, eqs. (7) reduce to the corresponding equations¹ for $f = 2$ {with $\tau^*/(f-2)^2 \rightarrow (k/2)\overline{[P_1]_0} \bar{\theta}$ and $\tau^*/(f-2) \rightarrow 0$ }.

Equation (7) can be simplified for the "steady-state nonperiodic" (denoted by subscript s) case when the feed to the HCSTR has a constant concentration $\overline{[P_1]_0}$ and when the $d/d\tau$ terms are all zero. This leads to

$$x_{1,0,s} = 1 \quad (9a)$$

$$x_{4,s} = 1 \quad (9b)$$

$$x_{3,s} = \left\{ 1 - 2\tau^* \left(1 + \frac{2}{f-2} \right) - \left[1 - 4\tau^* \left(1 + \frac{2}{f-2} \right) \right]^{1/2} \right\} / 2(\tau^*) \quad (9c)$$

$$x_{2,s} = \left\{ -1 - \frac{2\tau^*}{f-2} + \left[1 + \frac{4\tau^*}{f-2} \left(1 + \frac{2}{f-2} \right) \right]^{1/2} \right\} \left\| \left\{ \frac{4\tau^*}{(f-2)^2} \right\} \right. \quad (9d)$$

$$x_{1,s} = \left\{ 1 + \frac{\tau^* f}{f-2} \left(1 + \frac{2x_{2,s}}{f-2} \right) \right\}^{-1} \quad (9e)$$

which are consistent with our earlier results¹¹ for nonlinear polymerization, as well as with the results¹ for $f = 2$. Again, corresponding equations for random crosslinking of RA_f monomers can be written easily.

A common set of initial conditions which may be used for integrating the differential equations in eq. (7) can be written as

$$\begin{aligned} \text{IC1: } \tau = 0: & \quad (10) \\ x_1 = 1, \quad x_2 = 1, \quad x_3 = 0, \quad x_4 = 1 \end{aligned}$$

This would be the case when the HCSTR is filled with monomer at concentration $[\overline{P}_1]_0$ initially. An equally interesting initial condition (IC2) arises when the HCSTR is filled with pure solvent initially:

$$\begin{aligned} \text{IC2: } \tau = 0: & \quad (11) \\ x_1 = x_2 = x_3 = x_4 = 0 \end{aligned}$$

It is obvious that irrespective of the initial conditions, identical results will be obtained for x_i as $\tau \rightarrow \infty$

Equation (7d) for RA_f polymerization, for the dimensionless first moment, $\lambda_1/[\overline{P}_1]_0$, can be integrated analytically for IC1 as well as IC2. The following results are obtained:

For IC1:

$$x_4 = 1 + \frac{a}{1 + (\omega\bar{\theta})^2} \{ \sin(\omega\bar{\theta}\tau) - \omega\bar{\theta} \cos(\omega\bar{\theta}\tau) \} + \frac{a\omega\bar{\theta} e^{-\tau}}{1 + \omega^2\bar{\theta}^2} \quad (12a)$$

For IC2:

$$x_4 = 1 + \frac{a}{1 + \omega^2\bar{\theta}^2} \{ \sin(\omega\bar{\theta}\tau) - \omega\bar{\theta} \cos(\omega\bar{\theta}\tau) \} + \left(\frac{a\omega\bar{\theta}}{1 + \omega^2\bar{\theta}^2} - 1 \right) e^{-\tau} \quad (12b)$$

These can be substituted into eq. (7c) to give:

IC1 and IC2:

$$\frac{dx_3}{d\tau} = Ax_3^2 + B(\tau)x_3 + C(\tau) \quad (13a)$$

$$A = \tau^* \quad (13b)$$

$$B(\tau) = \frac{4\tau^*x_4}{f-2} + 2\tau^*x_4 - 1 \quad (13c)$$

$$C(\tau) = \tau^*x_4^2 \left\{ \frac{4}{(f-2)^2} + \frac{4}{f-2} + 1 \right\} \quad (13d)$$

with the appropriate expression for x_4 used from eq. (12). Equation (13a) is a Riccati equation¹⁴ and, since no general analytical solutions are readily available, it is best solved numerically.

RESULTS AND DISCUSSION

The final set of coupled differential equations [eqs. (7)] can be integrated numerically using the fourth-order Runge-Kutta method. Several checks have been made to ensure the correctness of the computer program. The numerically integrated results for x_4 [eq. (7d)] have been compared with their analytical counterpart [eq. (12)] for both the initial conditions IC1 and IC2. The two results are found to match up to the fourth decimal place for: (a) $f = 3$, $a = 0.8$, $\omega\bar{\theta} = \pi$, $\tau^* = 0.08$; (b) $f = 3$, $a = 0.8$, $\omega\bar{\theta} = \pi$, $\tau^* = 0.05$; and (c) $f = 3$, $a = 0.8$, $\omega\bar{\theta} = \pi/2$, $\tau^* = 0.08$. Several other cases also yielded identical results. In all the runs, the time period of oscillation was divided into 1000 steps for integration, i.e., $\Delta\tau = [2\pi/(\omega\bar{\theta})]/1000$. Reduction of the value of $\Delta\tau$ did not lead to any significant differences in the results. Further, results obtained numerically for IC1 and IC2 became identical at large values of τ .

Figures 2-5 give typical plots of how x_1 , x_2 , x_3 , and x_4 (which characterize the product properties) from the HCSTR, vary with the dimensionless time τ . Both IC1 and IC2 have been studied and the values of the dimensionless, independent parameters are $f = 3$, $a = 0.8$, $\omega\bar{\theta} = 2\pi$ (i.e., time period for

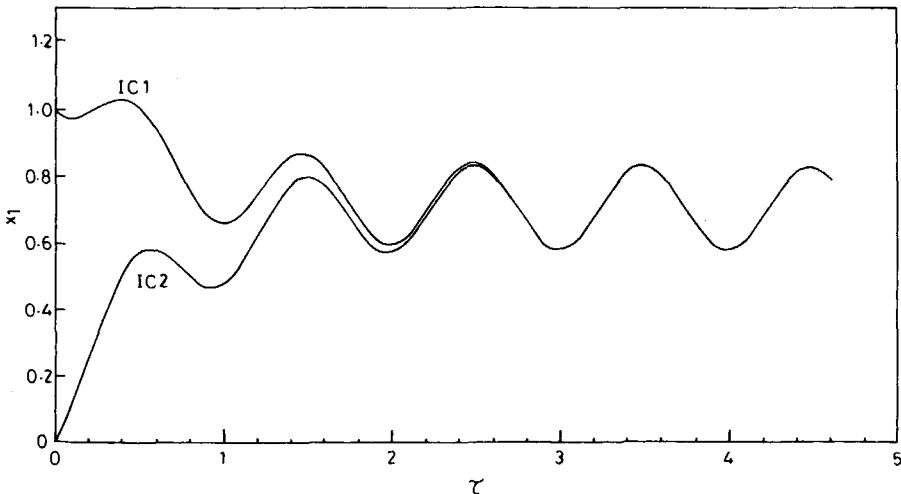


Fig. 2. $x_1(\tau)$ for IC1 and IC2: $a = 0.8$, $f = 3$, $\tau^* = 0.05$, $\omega\bar{\theta} = 2\pi$.

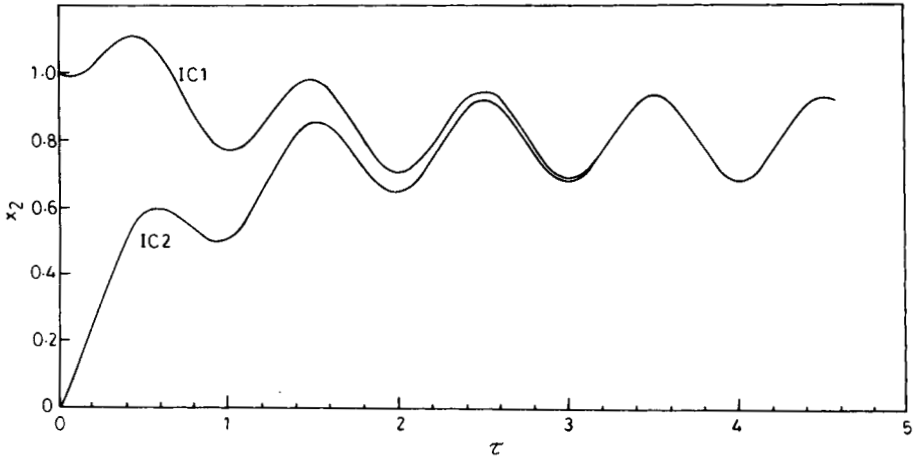


Fig. 3. $x_2(\tau)$ for IC1 and IC2. Conditions same as in Figure 2.

τ is 1), and $\tau^* = 0.05$. Similar results are also obtained for several other values of these independent parameters. It is observed that for τ less than about 10, the variables characterizing the output stream do not vary sinusoidally, and indeed, their amplitudes vary. However, after this initial "start-up" period, the values of x_1-x_4 vary sinusoidally with τ , with constant amplitudes. Thus, it takes some finite time for the reactor to attain *steady periodic* behavior. Also, both the ICs yield identical values of x_1-x_4 after the "start-up" period. For x_4 , eq. (12) also predicts such behavior since the terms involving $e^{-\tau}$ become negligible.

The behavior shown in Figures 2-5, in which a "start-up" period is fol-

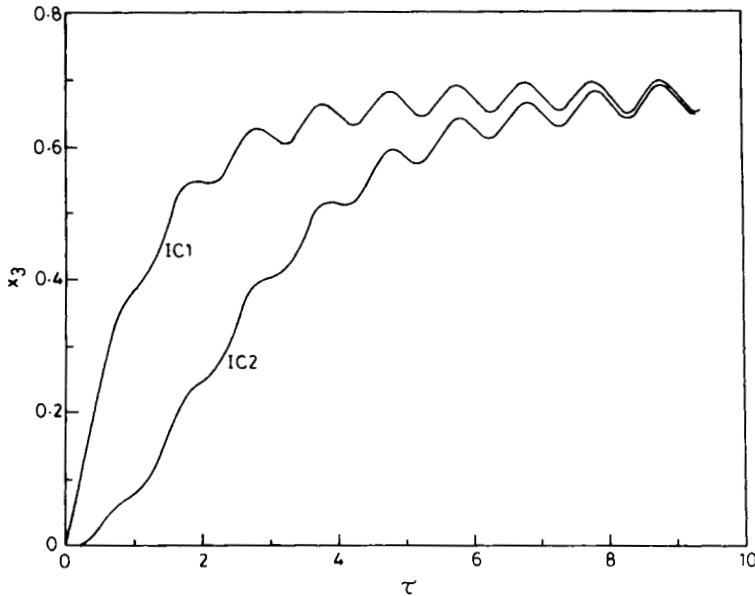


Fig. 4. $x_3(\tau)$ for IC1 and IC2. Conditions same as in Figure 2.

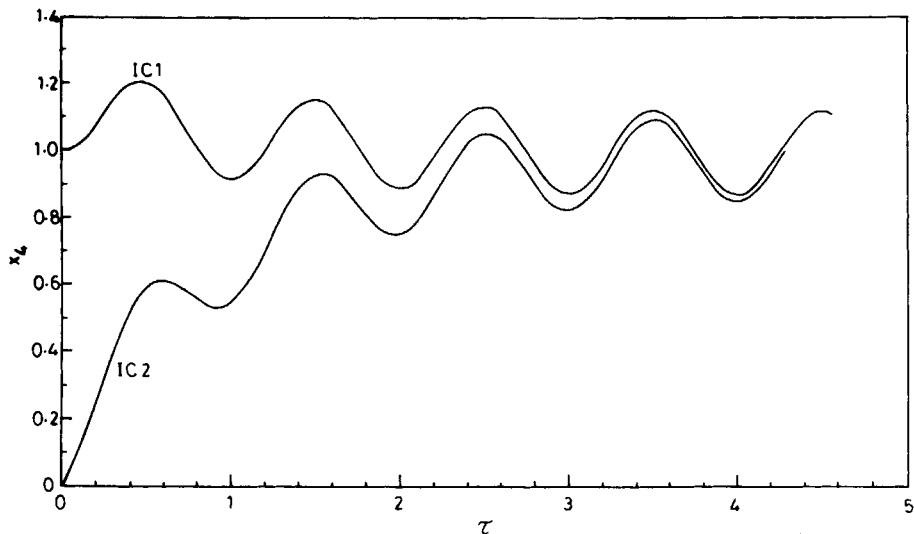


Fig. 5. $x_4(\tau)$ for IC1 and IC2. Conditions same as in Figure 2.

lowed by a steady periodic operation of the reactor, is found only for certain values of the independent parameters, f , a , $\omega\bar{\theta}$, and τ^* . For certain other combinations of these independent parameters, a "start-up" period is followed after some time, by gelation of the reaction mass with x_3 increasing progressively to infinity. Under such situations, steady periodic behavior is never realized, and HCSTRs are practically useless for polymerization.

It is difficult to predict with certainty, *in a numerical study such as this*, whether gelation will occur after a long time, and whether what is presumed as steady periodic behavior of an HCSTR is not really the beginning region of a delayed gelation. It was found, however, that for all cases of gelling encountered in this work, as the value of τ increases, the peak value, $x_{3,\max}$, of x_3 keeps on progressively increasing. In addition, the rate of increase of $x_{3,\max}$ increases with τ and very soon (e.g., at $\tau \simeq 75$ for $f = 3$, $a = 0.8$, $\omega\bar{\theta} = 2\pi$, $\tau^* = 0.085$), x_3 shoots up to 0.17×10^{39} , the maximum value permissible in the DEC 1090 computer. In contrast, in nongelling operation, the rate of increase of $x_{3,\max}$ does not increase with τ , even though the peak value itself may increase very slightly with τ because of accumulation of errors in the numerical procedure. This criterion is, therefore, used to infer whether one has gelling or nongelling operation of HCSTRs. To confirm this further, the numerical integrations were carried out to values of τ as high as 6000, and it was found that x_3 remained finite whenever the rate of increase of $x_{3,\max}$ does not increase with τ .

After establishing a suitable criterion for deciding whether gelation occurs or not in HCSTRs under periodic operation, attention was focused first on the operation of these reactors under nongelling conditions. The primary aim was to find out whether any advantage can be derived by operating the reactor in this mode. Thereafter, conditions under which gelation is encountered are explored, this information being useful to determine when it is worthwhile to use HCSTRs for RA_f polymerization.

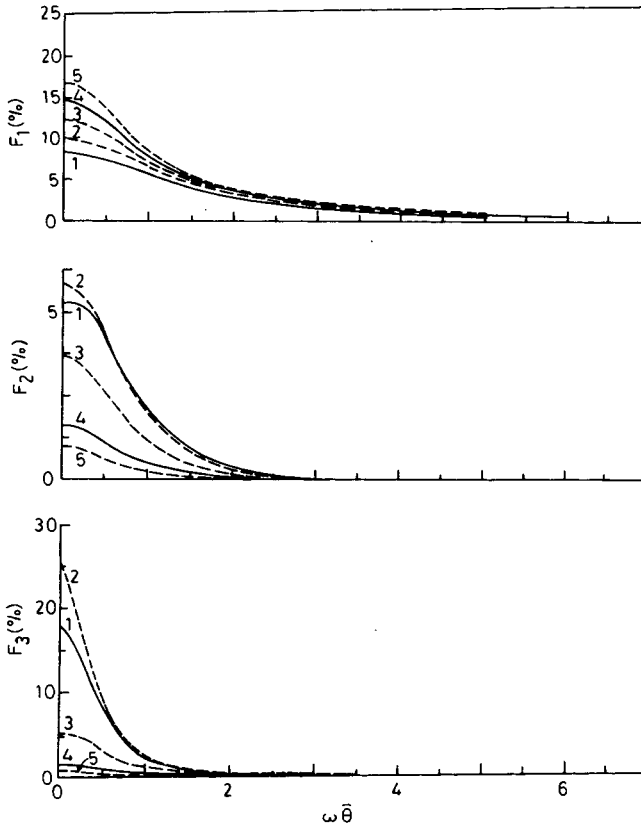


Fig. 6. F_1 , F_2 , and F_3 as a function of $\omega\bar{\theta}$ for $\alpha = 0.6$. Values of f and τ^* for the different curves are: (1) 3, 0.045; (2) 4, 0.075; (3) 4, 0.045; (4) 3, 0.01; (5) 4, 0.01.

To indicate the usefulness and increased flexibility that periodic operation gives to this system, Figures 6 and 7 have been drawn showing the effect of f , α , $\omega\bar{\theta}$, and τ^* on F_1 , F_2 and F_3 defined as

$$F_1 = \left(\frac{1 - \bar{x}_1}{1 - x_{1,s}} \right) \times 100 \tag{14a}$$

$$F_2 = \left(\frac{\bar{\mu}_n}{\mu_{n,s}} - 1 \right) \times 100 \tag{14b}$$

$$F_3 = \left(\frac{\bar{\rho}}{\rho_s} - 1 \right) \times 100 \tag{14c}$$

where

$$\bar{\mu}_n = (\bar{x}_4 - \bar{x}_1) / (\bar{x}_2 - \bar{x}_1)$$

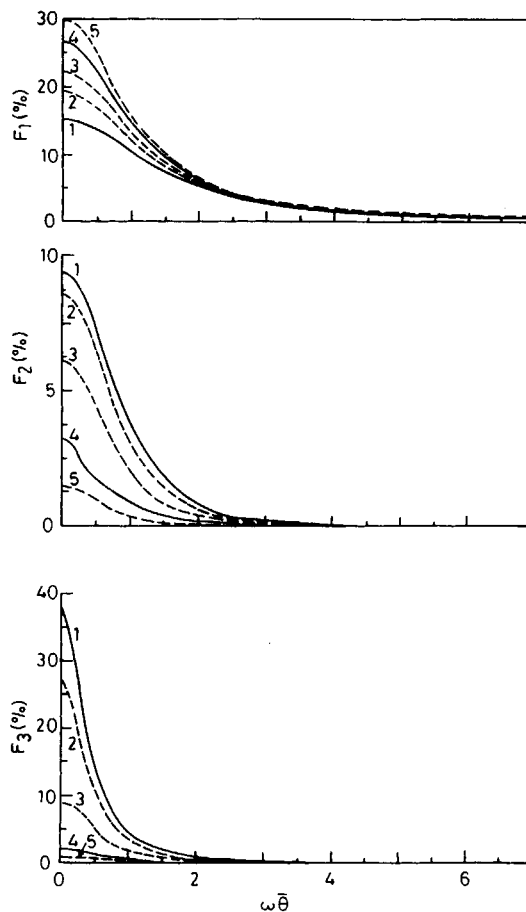


Fig. 7. F_1 , F_2 , and F_3 as a function of $\omega\bar{\theta}$ for $\alpha = 0.8$. Values of f and τ^* same as in Figure 5 for curves 1, 3, 4, and 5. For curve 2, $f = 4$, $\tau^* = 0.065$.

$$\begin{aligned}
 \mu_{n,s} &= (x_{4,s} - x_{1,s}) / (x_{2,s} - x_{1,s}) \\
 \bar{\mu}_w &= 1 + \{ \bar{x}_3 / (\bar{x}_4 - \bar{x}_1) \} \\
 \mu_{w,s} &= 1 + \{ x_{3,s} / (x_{4,s} - x_{1,s}) \} \\
 \bar{\rho} &= \bar{\mu}_w / \bar{\mu}_n \\
 \rho_s &= \mu_{w,s} / \mu_{n,s}
 \end{aligned}
 \tag{15}$$

These represent the change over nonperiodic (with $[P_1]_0$ constant with time at $[P_1]_0$) operation of the monomer conversion, number average chain length μ_n (with monomer excluded from summation), and the polydispersity index ρ (with monomer excluded), respectively.¹ The monomer was excluded from summations because it is generally flashed out from the monomer-polymer mixture. In the computation of $\bar{\mu}_n$ and $\bar{\mu}_w$, Simpson's rule was used to evaluate the average values of \bar{x}_i 's [eq. (8)] over one time period. The

Simpson's rule summations were performed after a sufficiently large value of τ to ensure steady, periodic behavior. It is observed from Figures 6 and 7 that the maximum deviations in F_1 , F_2 , and F_3 occur as $\omega\bar{\theta} \rightarrow 0$, and at high $\omega\bar{\theta}$, nonperiodic steady state behavior is approached, i.e., the reactor acts as a filter. Figures 6 and 7 show that for f and a remaining constant, F_2 and F_3 increase with τ^* . For the cases studied, an increase of as much as 37.5% in the polydispersity index and 8.5% in the number average chain length (for $f = 3$, $a = 0.8$, $\tau^* = 0.045$, $\omega\bar{\theta} \rightarrow 0$) is thus possible. F_1 , the percentage deviation in the monomer conversion, shows the reverse trend. An increase in a , the amplitude of oscillation, from 0.6 to 0.8 increases F_3 from about 18% to about 37.5%, other variables remaining constant. F_3 and F_2 fall from as much as about 35% to about 7.5% and from about 8% to about 5%, respectively, on increasing f from 3 to 4 for constant a and τ^* . This indicates the substantially increased flexibility possible in the operation of HCSTRs using periodic variation of the feed concentration.

Regions of gelling and nongelling operation and the effect of the variables f , a , and τ^* on these regions is shown in Figures 8 and 9. These regions were explored numerically for $f = 3$, $a = 0.6$ and 0.8 and $f = 4$, $a = 0.6$ and 0.8 for IC1. The numerical integrations were carried out till as high a value of τ as 8000 in some cases, in order to ensure that gelation does not occur. It is found that the gelling-nongelling envelope for periodic operation of HCSTRs can be described in terms of two critical dimensionless residence times, $\tau_{c,1}^*$ and $\tau_{c,2}^*$ defined by

$$\tau_{c,2}^* = \frac{0.25}{1 + 2/(f - 2)} \tag{16a}$$

$$\tau_{c,1}^* = \frac{\tau_{c,2}^*}{(1 + a)} \tag{16b}$$

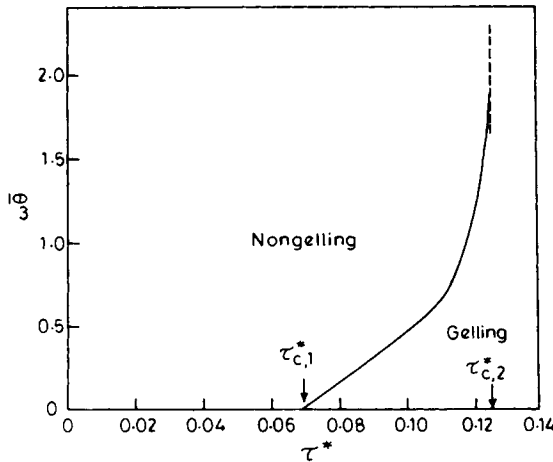


Fig. 8. Gelling-nongelling envelopes for $f = 4$, $a = 0.8$.

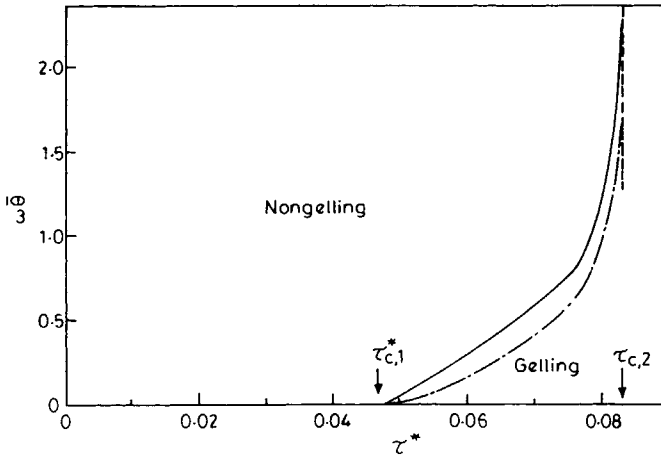


Fig. 9. Gelling-nongelling envelopes for $f = 3$, $a = 8$ (—) and $f = 3$, $a = 0.6$ (- · -).

When $\tau^* > \tau_{c,2}^*$ with periodic operation of HCSTRs, gelation always occurs irrespective of the value of a or $\omega\bar{\theta}$. If $\tau^* < \tau_{c,1}^*$ with periodic operation, nongelling operation is assured for all values of $\omega\bar{\theta}$. For $\tau_{c,1}^* \leq \tau^* \leq \tau_{c,2}^*$, it is found that gelation occurs below some value of $\omega\bar{\theta}$ while, above this value, nongelling behavior is guaranteed. Checks were made at several points in the regions $\tau_{c,1}^* < \tau^* < \tau_{c,2}^*$ and $\tau^* > \tau_{c,2}^*$ to determine the presence of any other localized gelling and nongelling regions. For $f = 3$, $a = 0.8$ and $\tau^* = 0.06$ and 0.08 (see Figs. 8 and 9), checks were made for 10 $\omega\bar{\theta}$ values ranging from 3 to 280 and at all these points the operation was indeed nongelling. Similar tests were made for $f = 3$, $a = 0.6$, $\tau^* = 0.05$ for $\omega\bar{\theta} = 1.0$ and 300. For $f = 3$, $a = 0.8$ and $\tau^* = 0.09$ and 0.12 [$\tau_{c,2}^* = 0.08333$ from eq. (16a)], the operation was gelling for $\omega\bar{\theta} = 5, 25$, and 45 . Thus, it is felt that the behavior depicted in Figures 8 and 9 is correct and a *single curve* separates the $\omega\bar{\theta} - \tau^*$ domain into gelling and nongelling regions.

It is interesting to observe that the two critical residence times, $\tau_{c,1}^*$ and $\tau_{c,2}^*$ for periodic operation of HCSTRs are related to the critical residence times for the case of nonperiodic steady state feed concentration, $\tau_{c,s}^*$, obtained earlier¹¹ as

$$\tau_{c,s}^* = (k/2)(f - 2)^2 [\overline{P_1}]_0 \bar{\theta}_{c,s} = \frac{0.25}{1 + 2/(f - 2)} \quad (17)$$

Thus, $\tau_{c,2}^*$ is the same as the critical residence time when an HCSTR operates with a constant feed concentration of $[\overline{P_1}]_0$, and it is intuitively obvious that gelation will definitely occur when $\tau^* > \tau_{c,2}^*$ irrespective of a and $\omega\bar{\theta}$. The other value, $\tau_{c,1}^*$ corresponds to the following critical condition when the feed concentration is constant with time at the peak value: $[\overline{P_1}]_0 (1 + a)$:

$$\frac{k}{2} (f - 2)^2 [\overline{P_1}]_0 (1 + a) \bar{\theta}_c = \frac{0.25}{1 + 2/(f - 2)} \quad (18)$$

which gives

$$\frac{k}{2} (f - 2)^2 \overline{[P_1]_0} \bar{\theta}_c = \left(\frac{0.25}{1 + 2/(f - 2)} \right) \frac{1}{(1 + a)} \quad (19)$$

This provides the lower limit of τ^* and it is not surprising that nongelling operation is ensured when $\tau_c^* < \tau_{c1}^*$.

This procedure was also used for the initial condition IC2 and it was seen that the gelling–nongelling envelope found for IC1 is valid for IC2 as well. Again this is intuitively obvious because after the initial settling time (~ 10 time periods in the case of Figs. 2–5), both the ICs give identical results for reactor performance.

CONCLUSIONS

The operation of HCSTRs using a sinusoidally varying feed concentration has been studied. A numerical criterion is first developed which establishes whether the reaction mass will ever gel or not. Values of the independent parameters are determined for which nongelling operation is ensured. Under these conditions, it is found that periodic operation can lead to higher values of monomer conversion, degree of polymerization as well as the polydispersity index.

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