Dynamics of Semibatch Polymerization Reactors: I. Theoretical Analysis

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The dynamics of semibatch reactors is often neglected in the literature despite their industrial importance. This article analyzes the stability and dynamic behavior of semibatch polymerization reactors operated according to a flow scheduling strategy designed to impart a steady-state nature to the dynamics of these essentially transient reactors. It can also improve the operation of these reactors, especially the quality of the polymer produced (such as molecular weight distribution and polymer composition). In the proposed strategy of flow rate scheduling, the intensive states of the reactor can be made to reach steady-state values. A comparison of the dynamics of the proposed and classical operating strategies illustrates this possibility. Further dynamic analysis reveals the emergence of phenomena characteristic of continuous operation in a CSTR. Examples are multiplicity of the trajectories, limit cycle oscillations, as well as nonhomogeneous oscillations belonging to a period doubling cascade. Operation in a sequential semibatch mode is discussed, as well as the importance of selecting parameters for the fillup and discharge operation. In this mode of operation either periodic or chaotic behavior is obtained. The effect of both on polymer properties is studied in detail.

Introduction

Continuous reactors are preferred in the chemical industry mostly because of their potential for good quality control and large production capacities. As an alternative, the semibatch mode of operation has proven to be very attractive for polymerization. Typically, this mode of operation does not require as much expertise for operation and maintenance as for the continuous mode. It also offers more flexible control capabilities on the quality of the polymer produced. For example, this type of operation can be advantageous in instances where the controlled addition of a comonomer or chain transfer agent is desired. It also allows for the use of different types of initiators at different stages of the polymerization process, which, with the availability today of such diverse multifunctional initiators, can be very attractive. The dynamic behavior of these reactors, however, has not been given as much attention as their continuous counterpart. In a previous study, Teymour and Ray (1989b) have proposed a flow rate scheduling technique that provides for improved operation of semibatch reactors and results in polymer properties comparable to those obtainable in a continuous stirred tank reactor (CSTR). This article explores the dynamics of semibatch reactors operated according to this technique and extends the analysis to the industrially important case of sequential semibatch operation.

The polymerization system studied by Teymour and Ray (1989b) is the free-radical solution polymerization of vinyl acetate, for which they analyzed the dynamic behavior in CSTRs in earlier publications (1989a, 1991, 1992a,b). In these studies, experimental and bifurcation analyses of a lab-scale reactor presented new evidence of limit cycle behavior for this system, and demonstrated the complexity and diversity of the structures existing in parameter space. Their bifurcation analysis of full-scale reactors revealed a higher degree of complexity that, among other things, materializes in the transition to chaotic behavior.

The analysis presented in this article demonstrates that if a proper strategy of inlet flow rate scheduling is used, the model equations for the semibatch reactor will resemble exactly those describing a CSTR. As a result, improved operation of semibatch reactors can be achieved, since their intensive states can be made to reach a steady-state equilibrium. Not surprisingly, along with the possibility of steady operation, all the potential stability problems and complex dynamic phenomena of the CSTR will be inherited in this scenario.

The analysis presented here for semibatch reactors also holds for the startup phase of a continuous tank reactor, which is transient in nature and often results in off-specifications product. The study of methods of improving the efficiency of such startup procedures can prove very beneficial, as will be shown later.

Dynamics of Semibatch Reactors

Literature on the dynamics and stability of semibatch reactors for general operation, as well as for polymerization, is very limited. Crowl (1987) reports on the behavior of a semibatch reactor for a catalyzed polyol process, but provides no details on the chemical system studied. Because of the special rate expression used for this polymerization process, one finds that if all the catalyst is initially charged to the reactor, the reaction rate can achieve a steady-state constant value. In other words, the effect of the continual addition of monomer on the reaction rate is found to be perfectly balanced by the continuous dilution of the catalyst as the reaction mass increases with time. Hence, a constant reaction rate can be achieved and, consequently, both the monomer conversion and temperature can reach steady-state values. His analysis locates a single steady state for these intensive properties, but finds a region in which the latter is unstable. Seemingly, at a Hopf bifurcation point the steady state gives way to a limit cycle. He reports only one dynamic simulation exhibiting oscillatory dynamics, which have the unique feature that the period of oscillation increases from cycle to cycle. This is caused by the fact that reaction mass—and consequently, the reactor time constant—is continuously increasing under the effect of the inlet flow rate. The motivation to Crowl's study presumably results from the experimental observation of these phenomena in a pilot-plant reactor, which suffered from temperature control problems during the monomer addition stage. It is thus obvious that stability problems for semibatch polymerization reactors are not a work of fiction, and that a better understanding of all dynamic possibilities is necessary.

In the case of the system studied here, Crowl's approach cannot be used since the rate of free radical polymerization depends on the concentration of both the monomer and the initiator. Also, the latter is consumed by reaction, as opposed to the true catalyst in Crowl's system. It will turn out, however, that through a suitable scheduling strategy in which the inlet flow rate is gradually increased as the reaction mass increases, such that the ratio of these two is kept constant, one can achieve steady-state operation. A similar feed program was proposed by Nauman (1970) when analyzing the transient behavior of stirred tank reactors in series in plants faced with variable production demands. However, this was not applied to an actual reaction system, and the issue of reactor dynamics was not analyzed.

A related but slightly different topic is that of designing monomer feed policies for copolymerization systems with the purpose of achieving a desired copolymer composition, usually not readily obtainable. Although the strategies presented here can be of practical value for copolymerization, only those polymer compositions obtainable in a CSTR can be duplicated in the semibatch reactor. For other modes of copolymer composition control, refer to the work of Hamielec and MacGregor (1983) and to the more recent publications by Canu et al. (1994) and Canegallo et al. (1994). Although the latter discusses composition control in emulsion copolymerization, which is considerably different from solution polymerization, it is interesting to note that the authors could achieve constant composition by requiring the feed policy to maintain a constant monomer concentration in the polymer particles, where the polymerization is taking place.

Reactor Model

The semibatch reactor model presented here is derived using the same approach as for the CSTR model of Teymour and Ray (1992b). In this semibatch mode all components of the reaction mixture are fed simultaneously to an initially empty (or partially full) reactor. The resulting equations display a structure similar to that of the CSTR model, except that no outflow term appears for the semibatch reactor case and that the states of the latter explicitly depend on the volume of the reaction mixture, which by definition is continuously varying. Thus, a dynamic total reactor volume balance is necessary. This is formulated as follows:

Rate of change of total reactor volume =
Volumetric inflow corrected to reactor temp. +
Rate of vol. change due to polymerization +
Rate of vol. change due to thermal effects

and can be expressed as

$$\frac{dV}{dt} = q\frac{\rho_f}{\rho_{f(T)}} + V[MW]_m\,\mathcal{R}_m\left[\frac{1}{\rho_p} - \frac{1}{\rho_m}\right] - V\sum_i \frac{\nu_i}{\rho_i}\frac{d\rho_i}{dt} \tag{1}$$

The monomer and solvent balances are expressed in terms of volume fractions to allow for the direct incorporation of density change effects into the model. $[MW]_m$ is the molecular weight of monomer (gm/mol). $\mathcal{R}_m$ is the rate of consumption of monomer (mol/L·min). ρ is the density of reaction mixture (gm/L), and ρ_f is the density of feed (gm/L). $\rho_{f(T)}$ is the density of feed adjusted to reactor temperature (gm/L).

In order to illustrate the procedure used in deriving the model equations, the monomer balance will be used with the understanding that the extension to the remaining equations is straightforward. A volume balance on the monomer is first expressed in terms of the partial volume of monomer v_m as follows

$$\frac{dv_m}{dt} = \varphi_m q\frac{\rho_{mf}}{\rho_m} - V\frac{[MW]_m}{\rho_m}\mathcal{R}_m - \frac{v_m}{\rho_m}\frac{d\rho_m}{dt} \tag{2}$$

Equation 2 is then expressed in terms of the monomer volume fraction ν_m, ($\nu_{m,s}$ is volume fraction of monomer, solvent in reactor) using the differential relation

$$\frac{dv_m}{dt} = V\frac{d\nu_m}{dt} + \nu_m\frac{dV}{dt} \tag{3}$$

which results in

$$\frac{d\nu_m}{dt} = \varphi_m\left(\frac{q}{V}\right)\frac{\rho_{mf}}{\rho_m} - \frac{[MW]_m}{\rho_m}\mathcal{R}_m - \frac{\nu_m}{\rho_m}\frac{d\rho_m}{dt} - \frac{\nu_m}{V}\frac{dV}{dt} \tag{4}$$

The similarity between Eq. 4 and its equivalent in the CSTR model of Teymour and Ray (1992b) becomes clear when one notices that the outflow term of the CSTR is replaced by a term representing the dilution effect resulting from the reactor volume dynamics. This term is expressed in Eq. 1, which can be seen to resemble the outlet flow rate equation of the CSTR model. Another observation that is important for the present analysis is that the reactor volume always appears in the ratio q/V, as in the monomer balance (Eq. 4), or in the volume balance (Eq. 1) after dividing its terms by V.

Case 1: constant inflow

As mentioned earlier, the goal of this study is to analyze a suggested flow rate scheduling strategy that will result in an improved operation for the semibatch reactor. For the purpose of comparison, however, the case of constant feed flow rate will be first considered, since it is currently used in some form or other in most instances of semibatch polymerization. For this case, all the reactor properties are clearly dynamic in nature, since the model equations depend on the reactor volume, which by definition is not constant. The model equations will be scaled using the characteristic time constant $\hat{\theta}$ (min) defined by

$$\hat{\theta} = \frac{V_f}{q} \tag{5}$$

where V_f is the final reactor volume, which was chosen as a reference to compare the results of this case and of the scheduled inflow case to the dynamics of a CSTR of constant volume V_f. A dimensionless reactor volume variable ω is also used and is defined as V/V_f. It is further assumed that the design of the reactor is such that the heat-transfer area increases at a rate proportional to the reactor volume increase, which is the case for cylindrical jacketed reactors, or for reactors fitted with immersed cooling coils that span the full range of variable volume in the reactor. The use of this assumption will result in a dimensionless overall heat-transfer coefficient term that is independent of the reactor volume, and is necessary for the development of the equations of the case 2 reactor. The dimensionless heat-transfer coefficient B is defined as in the product

$$\alpha B = \frac{UA}{V} \tag{6}$$

$\alpha = (\rho c_p)_{\text{ref}}/\theta_{\text{ref}}$. θ is CSTR residence time (min). UA is the overall heat-transfer coefficient (cal/min·°C). The resulting model equations are summarized in Table 1.

Table 1. Semibatch Reactor Model for Case 1

$$\begin{aligned}
\frac{d\nu_m}{d\tau} &= \frac{(1-\varphi_s)}{\omega}\frac{\rho_{m_f}}{\rho_m} - \nu_m\left(\frac{1}{\omega}\frac{d\omega}{d\tau}\right) - \hat{\theta}\nu_m(k_p + k_{trm})P \\
&\quad - \hat{\theta}\frac{[MW]_m}{\rho_m}2fk_d z_i I_f - \frac{\nu_m}{\rho_m}\frac{d\rho_m}{d\tau} \\
\frac{d\nu_s}{d\tau} &= \frac{\varphi_s}{\omega}\frac{\rho_{s_f}}{\rho_s} - \nu_s\left(\frac{1}{\omega}\frac{d\omega}{d\tau}\right) - \frac{\nu_s}{\rho_s}\frac{d\rho_s}{d\tau} \\
\frac{dz_i}{d\tau} &= \frac{1}{\omega} - \hat{\theta}k_d z_i - z_i\left(\frac{1}{\omega}\frac{d\omega}{d\tau}\right) \\
\frac{dy}{d\tau} &= \left\{\frac{\rho_f c_{p_f}}{\omega\rho c_p}(y_f - y_{\text{ref}}) - \frac{\rho_f}{\omega\rho}(y - y_{\text{ref}})\right. \\
&\quad \left. + \frac{-\Delta H_R}{\rho c_p T_c}\hat{\theta}\nu_m k_p \frac{\rho_m}{[MW]_m}P - \hat{\theta}\,\frac{\alpha B}{\rho c_p}(y-1)\right\} \\
\frac{1}{\omega}\frac{d\omega}{d\tau} &= \frac{1}{\omega}\frac{\rho_f}{\rho_{f(T)}} + \hat{\theta}[MW]_m\,\mathfrak{R}_m\left[\frac{1}{\rho_p} - \frac{1}{\rho_m}\right] - \sum_i \frac{\nu_i}{\rho_i}\frac{d\rho_i}{d\tau}
\end{aligned}$$

Case 2: inlet flow rate scheduling

The selection of a flow rate scheduling strategy that will achieve the desired goal of approximating a CSTR behavior when operating in semibatch mode takes advantage of the earlier observation that the reactor volume only appears in the material balance equations in the ratio V/q, for example, as in Eq. 4. It is clear then that if one adopts an open-loop strategy in which this ratio is kept constant that in essence all the reactor states, except the volume, can reach a steady state. In the resulting mode of operation, the extensive state of the system would continuously change, while the intensive states would converge onto an attractor in the phase plane.

The derivation of the model equations for this operating strategy makes use of a time constant $\hat{\theta} = V/q$, which is different from that used for case 1, but tends to the same limiting value of the equivalent CSTR residence time as the reactor fills up. The resulting model equations are presented in Table 2.

Table 2. Semibatch Reactor Model for Case 2

$$\begin{aligned}
\frac{d\nu_m}{d\tau} &= (1-\varphi_s)\frac{\rho_{m_f}}{\rho_m} - \nu_m\left(\frac{1}{V}\frac{dV}{d\tau}\right) - \hat{\theta}\nu_m(k_p + k_{trm})P \\
&\quad - \hat{\theta}\frac{[MW]_m}{\rho_m}2fk_d z_i I_f - \frac{\nu_m}{\rho_m}\frac{d\rho_m}{d\tau} \\
\frac{d\nu_s}{d\tau} &= \varphi_s\frac{\rho_{s_f}}{\rho_s} - \nu_s\left(\frac{1}{V}\frac{dV}{d\tau}\right) - \frac{\nu_s}{\rho_s}\frac{d\rho_s}{d\tau} \\
\frac{dz_i}{d\tau} &= 1 - \hat{\theta}k_d z_i - z_i\left(\frac{1}{V}\frac{dV}{d\tau}\right) \\
\frac{dy}{d\tau} &= \left\{\frac{\rho_f c_{p_f}}{\rho c_p}(y_f - y_{\text{ref}}) - \frac{\rho_f}{\rho}(y - y_{\text{ref}})\right. \\
&\quad \left. + \frac{-\Delta H_R}{\rho c_p T_c}\hat{\theta}\nu_m k_p \frac{\rho_m}{[MW]_m}P - \hat{\theta}\,\frac{\alpha B}{\rho c_p}(y-1)\right\} \\
\frac{1}{V}\frac{dV}{d\tau} &= \frac{\rho_f}{\rho_{f(T)}} + \hat{\theta}[MW]_m\,\mathfrak{R}_m\left[\frac{1}{\rho_p} - \frac{1}{\rho_m}\right] - \sum_i \frac{\nu_i}{\rho_i}\frac{d\rho_i}{d\tau}
\end{aligned}$$

In the suggested inlet flow rate scheduling protocol, $\hat{\theta}$ is kept constant by increasing the feed rate to the reactor as its volume increases. When this is achieved, the equations of the model for the intensive states become independent of the reactor volume, as clear from the equations of Table 2. Moreover, the equations become identical to those describing the full-scale CSTR of Teymour and Ray (1992b), with the volume derivative term $1/V\ (dV/d\tau)$ replacing the flow rate ratio term used there. As a result, the intensive states of the

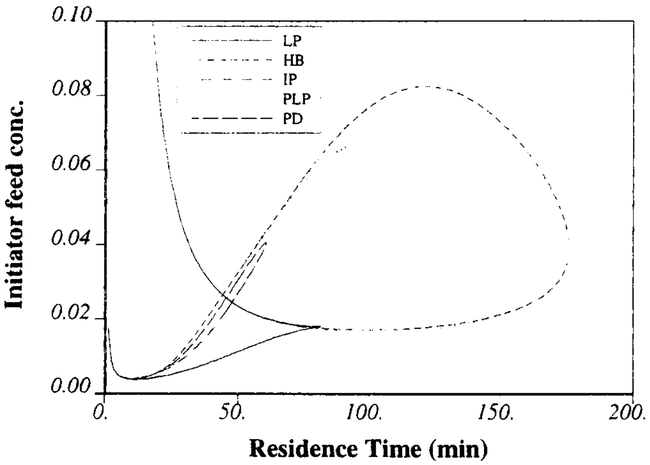

Figure 1. Bifurcation structure diagram tracing the loci of special points, including limit points (LP), Hopf bifurcations (HB), orbits of infinite period (IP), periodic limit points (PLP), and period doubling (PD) bifurcations.

After Teymour and Ray (1992b).

semibatch reactor will exhibit the same dynamic behavior as those of the CSTR. Consequently, the results of the CSTR bifurcation analysis are valid for the case 2 reactor studied here, and, for example, the bifurcation structure diagram of Figure 1 will be indicative of the steady state and dynamic behavior to be expected in specific portions of the selected parameter space.

Results and Discussion

Three different applications of the semibatch mode of operation are considered in this section. The first application is to the dynamics of a large industrial semibatch reactor, while the second is concerned with the startup phase of a CSTR. The last application analyzes the sequential operation mode in which successive semibatch runs are carried out in order to meet certain production requirements. For each application, I will demonstrate the usefulness of the flow rate schedule proposed here in improving the quality of polymer produced; then, I will analyze the possible dynamic complexities that might result from operation under "steady" conditions.

Single semibatch reactor

In some industrial installations, a large reactor is used in semibatch mode to produce a certain polymer grade, then, other grades or formulae are made in subsequent runs. Both strategies discussed earlier for the operation of such a reactor are considered here.

Operation with a constant reactor inflow (case 1) is expected to result in time varying properties. Moreover, as seen from the equations of the model (Table 1) the dynamic behavior should depend largely on ω as well as $\hat{\theta}$. However, the dependence on the latter is greatly diminished by the fact that the reactor volume increases rapidly as the reactor fills up. As a result, the dynamic time profiles seem almost unaffected by the value chosen for this characteristic time constant, and hence are almost independent of the inlet flow rate used. Results suggest that, depending on the initial value chosen, there exists a family of curves that all fall along the same trajectory. If, instead, the property profiles are plotted against the reactor volume, these are found to be shifted apart depending on the value used for $\hat{\theta}$, as illustrated in Figure 2. The profiles still retain the same general shape, but occur at different reactor volume values. It becomes clear from Figure 2 that very low flow rates have to be used before one could observe a considerable level of conversion at a reasonable reactor volume. It is also clear that the monomer conversion —and the same is true for temperature—never reaches a "steady" state.

In contrast, the protocol of flow rate scheduling suggested for the case 2 reactor will result in a mode of semibatch operation capable of achieving steady-state operation, in which the intensive reactor properties are time invariant. This, however, entails the possibility of dynamic instabilities, as observed for the CSTR system. In what follows, the reactor dynamics are analyzed in various regions of parameter space, where different types of interesting behavior are observed. These were located with the help of the diagram of Figure 1. One has to be cautious, however, when analyzing the dynamics of semibatch reactors, since these cannot be run indefinitely as assumed for CSTRs. Since the reactor volume increases with time, one has to insure that it stays within reasonable limits at all times. The analysis of this section will limit the final reactor volume to 25,000 L, which is at the upper limit of common reactor sizes for similar applications. The reactor is always assumed empty initially, but in order to avoid the singularity resulting at $V = 0$, a very small value (typically 1 L) is used as the initial condition for reactor volume. Under these conditions, the resulting reactor fill up time will be approximately ten times the corresponding CSTR residence time. In practice, however, the reactor will first be precharged with a given percentage of its total volume, thus cutting down the required time by a considerable margin. This idea is applied later for the case of successive semibatch runs. Conditions used for the analysis are presented in Table 3, except for I_f and $\hat{\theta}$ which are reported along with each simu-

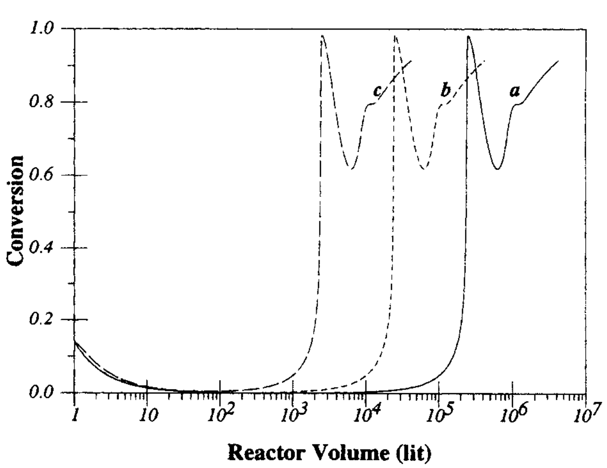

Figure 2. Conversion dynamics for case 1, plotted vs. volume in reactor.

(a) $\hat{\theta} = 10$ min; (b) 100 min; (c) 1,000 min.; general profile shape is almost invariant.

Table 3. Reactor Conditions Used in Analysis

$T_c = 45°C$
$T_f = 30°C$
$\varphi_s = 0.6$
$B = 1.4$
$\theta_{\text{ref}} = 60$ min
$(\rho c_p)_{\text{ref}} = 1{,}000$ cal/L·°C

lation. The kinetic rate constants are representative of the vinyl acetate polymerization system as reported by Teymour and Ray (1989a).

The first phenomenon observed for the semibatch reactor in question is that of the multiplicity of the steady state, a property not observed previously for this class of reactors. This multiplicity behavior is exhibited in Figure 3, where it could be seen that when the initial reactor temperature was equal to the feed temperature, the reactor converged to a low conversion "steady" state; whereas, when the feed was introduced into a reactor preheated to 90°C, the final state obtained could be seen to fall on the upper solution branch. (I is the initiator concentration in reactor, mol/L, and I_f is the initiator feed concentration, mol/L.) Figure 3 demonstrates that the anticipated possibility of operating at a "steady" state has been proven possible; it is also important to note that the initial transient period, despite representing approximately 1/5 of the reactor fill up time for the case discussed, in reality has a much smaller effect on the polymer quality produced. This is caused by the fact that under this feed protocol the reactor volume increases exponentially, and that most of the inflow addition occurs in the later stage of the fill up operation, after the intensive states have reached a steady state. This is illustrated in Figure 4, where the exponential rate of increase of the volume is apparent, and where it could also be noticed that on the way to either one of two totally different final states, the reactor fills up following almost identical trajectories. On its way to the low conversion steady state, the reactor fills up slightly faster, since no appreciable volume contraction would be sensed. To illustrate the point made earlier about these transients, one can simulate their effect on polymer properties, as in Figure 5, in which the weight-average molecular weight and the polydispersity of the polymer are presented. It can be seen that, although polymer with a broad molecular weight distribution is produced during the early stages, the final polydispersity of the polymer approaches 2.0, which is the same value expected from a CSTR. Details about the polymer property modeling are presented by Teymour (1989). Also, the molecular weight quickly converges to the corresponding value for a CSTR. Obviously, the effect of the early temperature transients is negligible because these are over before any considerable amount of material has been fed to the reactor.

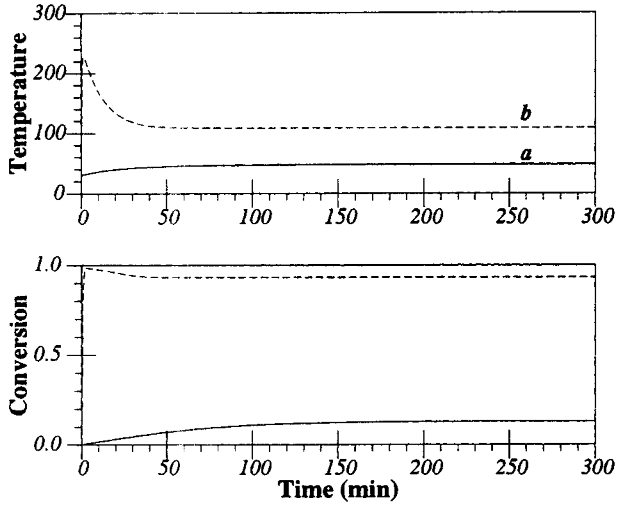

Figure 3. Temperature and conversion dynamics for case 2, exhibiting multiplicity of the steady state.

(a) Initial reactor temperature is T_f (K); (b) reactor preheated to 90°C. $I_f = 0.04$ mol/L, $\hat{\theta} = 30$ min.

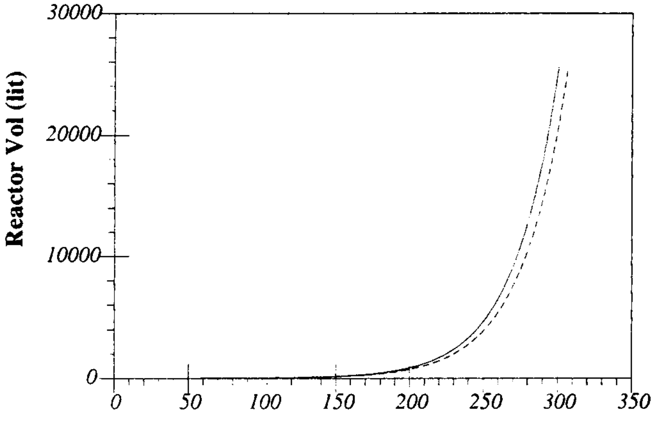

Figure 4. Reactor volume dynamics for the simulation of Figure 3.

The dynamic behavior of the reactor studied, as indicated by Figure 1, also encompasses oscillatory dynamics, which is a similar behavior to that observed by Crowl (1987), but oc-

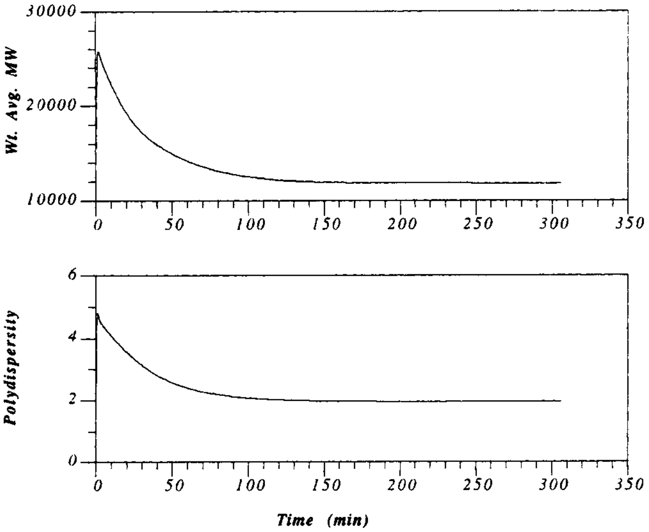

Figure 5. Dynamic behavior of polymer properties for the case of the high temperature steady state of Figure 3.

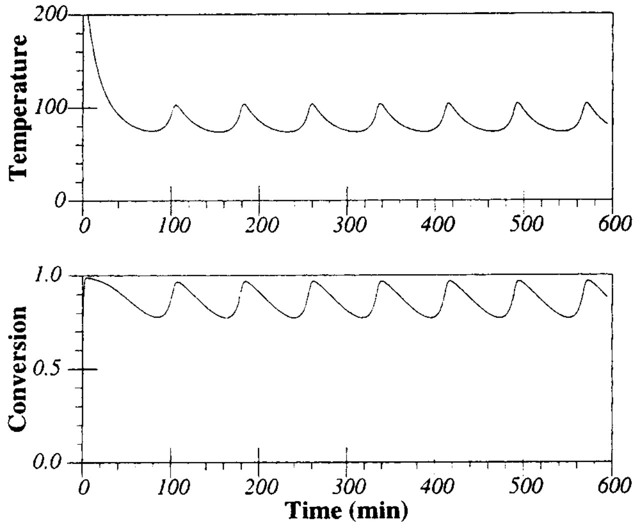

Figure 6. Temperature and conversion dynamics for case 2, exhibiting a small amplitude limit cycle.

$I_f = 0.04$ mol/L, $\hat{\theta} = 57$ min.

curs here with constant period. This is caused by the fact that here the reactor is operated at a constant characteristic time, and hence approaches the behavior of a CSTR. Examples of oscillatory behavior are presented in Figures 6 and 7. At relatively short residence times, as in Figure 6, small amplitude oscillations are observed, while at longer residence times sharp peaked long period cycles can be seen as in Figure 7.

As for the case of the CSTR analyzed by Teymour and Ray (1992b), the semibatch reactor studied here is capable of exhibiting even more complex oscillations, including chaotic ones. Because of the final volume constraint, however, only a limited number of cycles of any oscillatory regime can be observed, which limits the possibility of analysis of chaotic phenomena for these reactors, since these become indistinguishable from orbits of high periodicity. It suffices here to show that the reactor dynamics are capable of undergoing oscillations exhibiting multipeaked cycles, as a statement of the higher degree of complexity of the periodic behavior that could be expected there. Figure 8 illustrates this point with a period doubling bifurcation onto an orbit of periodicity 2.

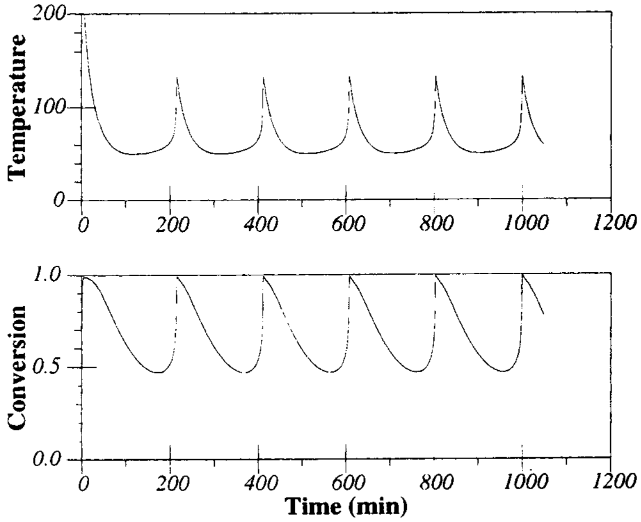

Figure 7. Temperature and conversion dynamics for case 2, exhibiting large amplitude oscillations.

$I_f = 0.04$ mol/L, $\hat{\theta} = 100$ min.

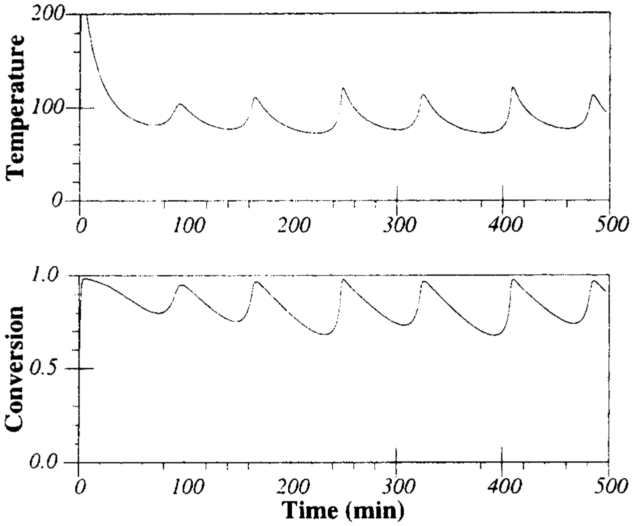

Figure 8. Temperature and conversion dynamics for case 2, exhibiting period doubling behavior.

$I_f = 0.028$ mol/L, $\hat{\theta} = 48$ min.

CSTR startup

Another instance in which the semibatch mode is necessary is during the startup of a CSTR after a shutdown. The reactor is initially empty, and is filled with the material until it overflows, at which point continuous operation is possible. Usually, the reactor will be filled at a constant inflow at the same rate used for continuous operation. This mode, however, as seen earlier, will result in considerable transience and consequently a large amount of off-specification polymer. The use of the flow rate schedule proposed for case 2 will minimize such effects as it operates mostly at steady state.

Since most of the time, the desired operation of a CSTR would be at a stable steady state, that is where the performance of the two strategies is compared. Figure 9 presents the results of dynamic simulations for both startup protocols at a relatively short CSTR residence time, and seems to indicate that their performances are comparable, since they settle down at about the same time with the case 2 protocol being slightly faster to equilibrate. However, the temporal dynamics can be deceiving, since what counts most is not the elapsed time during the stage of off-specification production, but the off-specification material produced during startup. Since the case 2 reactor fills up exponentially as opposed to the linear fill up of the case 1 reactor, it is started at a very low inlet flow rate, which is then increased in proportion to the volume increase. As a result, the fill up periods of both reactors are vastly different. This is illustrated in Figure 10, where it can be seen that by the time the dynamics of the case 2 reactor settle down it is less than 3% full, whereas the case 1

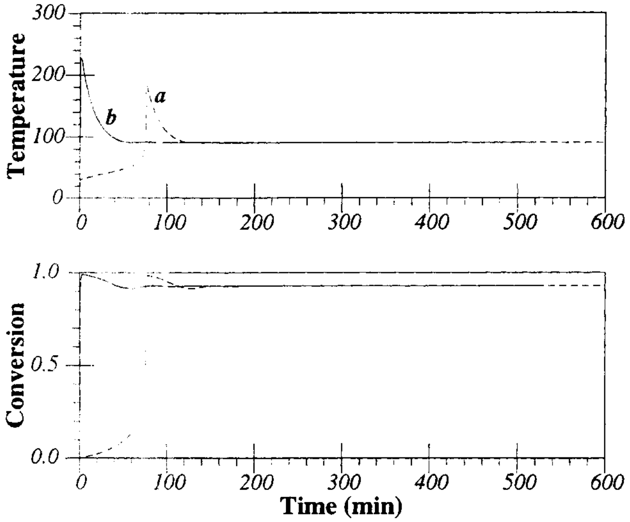

Figure 9. Comparison of temperature and conversion dynamics for (a) case 1; (b) case 2 protocols.

I_f = 0.06 mol/L, $\hat{\theta}$ = 50 min.

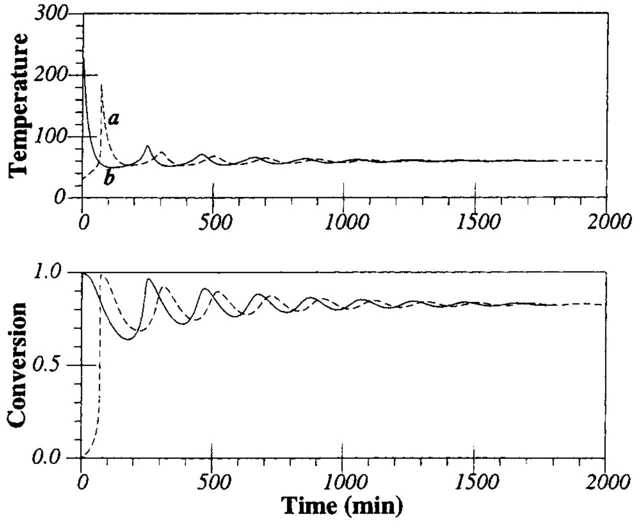

Figure 11. Comparison of temperature and conversion dynamics for (a) case 1; (b) case 2 protocols.

I_f = 0.065 mol/L, $\hat{\theta}$ = 180 min.

reactor has already processed the equivalent of 2.5 reactor volumes before the—now full—CSTR reaches a stable operation. The protocol suggested here is clearly much more efficient as far as avoiding product waste is concerned, however, it requires a much longer startup time, generally of the order of 10 reactor residence times. The value of startup time has to be weighted against the product quality before a decision can be made in favor of either protocol. However, as suggested earlier, different variations of the case 2 protocol involving different amounts of reactor precharge will result in considerable savings in fill up time, often without much effect on the polymer properties. This is illustrated in more detail in the next section.

A comparison of cases 1 and 2 behavior can also be made at a longer residence time where the reactor dynamics are damped oscillatory—cf. Figure 11, and again it can be seen that although the dynamic settling rates of both reactors are comparable, the amount of generated off-quality product is much less for the protocol of case 2.

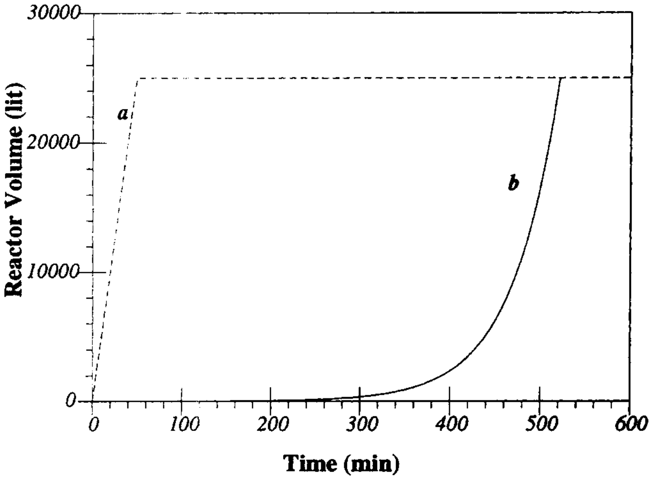

Figure 10. Comparison of fill up times for (a) case 1; (b) case 2 protocols.

I_f = 0.06 mol/L, $\hat{\theta}$ = 50 min.

Sequential semibatch operation

In some installations, the volume of production is not large enough to justify continuous operation, yet some product grades are needed in volumes much larger than the size of the available reactor. Under these conditions, sequential semibatch operation is normally used. The product from each cycle is usually sent to an intermediate storage step prior to downstream processing. Each reactor filling and emptying cycle could be run at constant feed inflow and product withdrawal rates, however, the resulting polymer quality will be inferior to that produced in a CSTR because of the time varying nature of this mode of operation. I have shown earlier that one could approximate CSTR operation in a single semibatch run, and attempt here to extend this advantage to successive operation. This section will analyze the cyclic operation mode in which the reactor is filled under the same feed protocol of case 2, then partially emptied at a constant yet fast rate of product withdrawal. This will represent cycles of exponential filling followed by fast linear partial emptying of the reactor vessel. As before, it is expected that the reactor intensive states will get to a steady state during filling. The additional premise is that the disturbance in these states resulting from the transient nature of the emptying stage can be minimized by the proper choice of the parameters for each cycle. This fact is first demonstrated, followed by an analysis of the complex dynamics that might result in this forced mode of operation.

The conditions used for CSTR startup (Figure 9) will be used as the basis for this analysis. In all cases, the reactor will be assumed virtually empty at the start of the first cycle, then the reactor will be filled to a maximum value of 5,000 L. This represents a relatively small reactor, as would be expected under the above described scenario. Subsequent cycles will start from a partially filled reactor; as pointed out earlier, this should result in considerable savings in processing time. The minimum holdup volume will be considered one of the parameters characterizing the forcing cycle, in addition to the rate of product withdrawal. For each case, two values are reported: the minimum holdup as a percentage of the total reactor volume, and the discharge ratio γ defined as the ratio of the emptying time to the characteristic time $\hat{\theta}$.

Figure 12 illustrates this mode of operation when the minimum holdup was 5% of the reactor volume and the discharge time was one-tenth of the characteristic time. It can be observed that the first cycle is considerably longer than subsequent cycles, and that by its end the reactor is at steady state. Oscillatory excursions in temperature and conversion are observed in the beginning of each additional cycle, but these settle down near the end of the cycle. As a result, both the polymer molecular weight and its polydispersity are seen to increase initially in each cycle; then, they decrease until they reach their steady-state values. The polydispersity approaches its desired value of 2.0, and the polymer collected after each cycle is of quality equivalent to the quality of polymer manufactured in a CSTR.

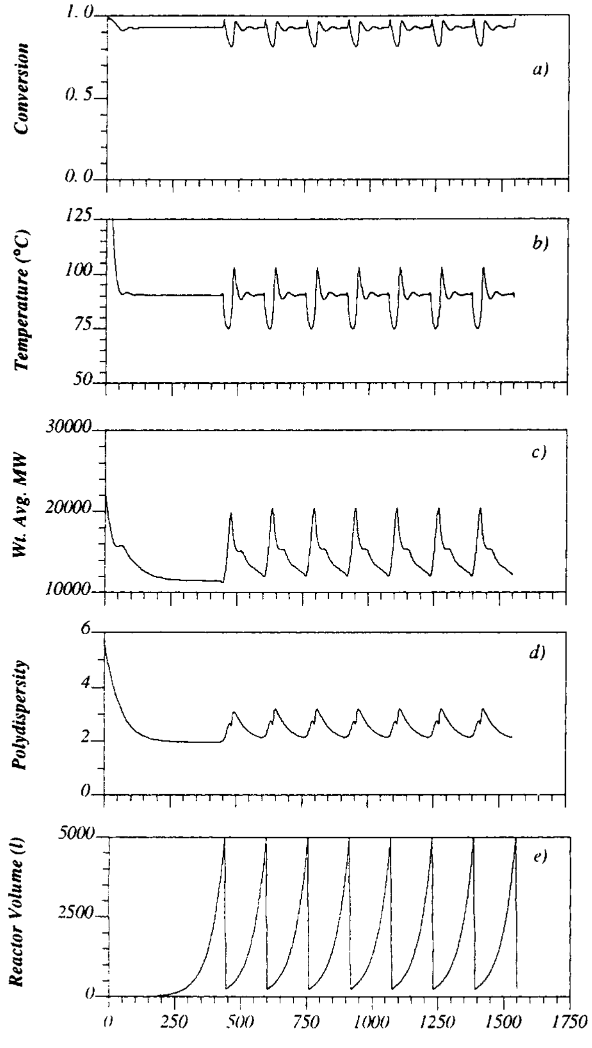

Figure 12. Dynamics of sequential semibatch operation.

$I_f = 0.06$ mol/L, $\hat{\theta} = 50$ min, minimum holdup 5%, discharge ratio $\gamma = 0.1$. (a) conversion; (b) temperature; (c) weight avg. MW; (d) polydispersity; (e) reactor volume.

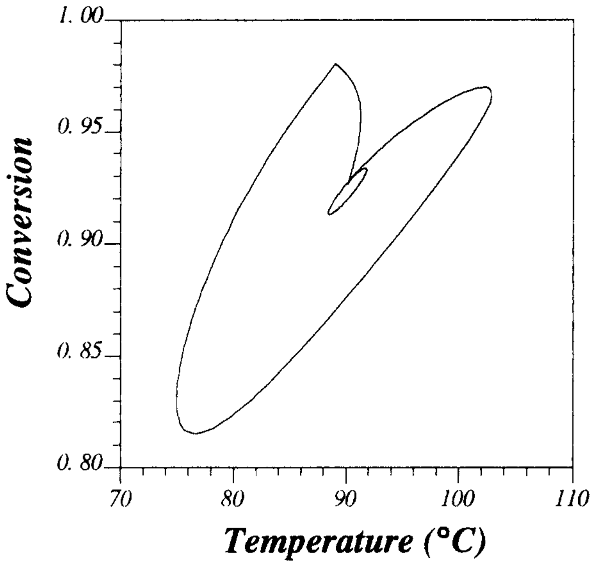

Figure 13. Phase plane illustrating the limit cycle attractor of Figure 12.

It can be seen that the forcing function consisting of a reactor filling followed by emptying has caused the originally stable steady state to bifurcate onto a limit cycle, and thus resulted in the periodic dynamics seen in Figure 12. However, the transient nature of the emptying part of the cycle causes some decaying oscillations in the beginning of each cycle resulting in a complex shape for the limit cycle in the phase plane as seen in Figure 13, where the monomer conversion is plotted vs. temperature.

The parameters of the forcing cycle in Figure 12 have been chosen to yield acceptable polymer quality, however, other choices might not be adequate. To avoid this possibility, the effects of both the minimum holdup and the rate of reactor product withdrawal have to be fully understood. Figure 14 illustrates the effect of increasing the minimum holdup to 20% of the reactor volume. It can be observed that the deviations in polymer properties are now smaller since the cycle time is shorter. However, this also implies that the reactor has less time to recover from the recurring transient disturbance, and, consequently, it never returns to its original steady state. Figure 14 shows that the polymer molecular weight at the end of each cycle is considerably larger than its corresponding value at the end of the first cycle, and that the polydispersity is larger than 2.0. The effect of minimum holdup is summarized in Table 4. Alternatively, the effect of varying the discharge rate is illustrated in Figure 15 which shows that when the reactor is emptied in twice the time it took for the case of Figure 12, larger excursions in reactor states and polymer properties resulted and that the polydispersity still finished at a value higher than 2.0. The effect of various discharge rates is summarized in Table 5.

To understand the combined effect of these two parameters, one has to follow the reaction during each cycle. At the end of each fill up, the emptying stage represents the equivalent of a batch holdup period, during which additional polymerization occurs. The longer that operation takes, the closer

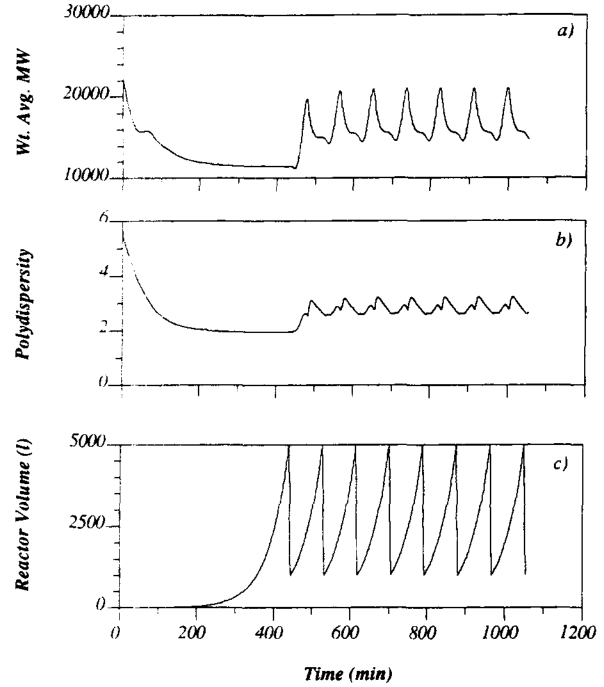

Figure 14. Dynamics of sequential semibatch operation.

$I_f = 0.06$ mol/L, $\hat{\theta} = 50$ min, minimum holdup 20%, discharge ratio $\gamma = 0.1$. (a) Weight avg. MW; (b) polydispersity; (c) reactor volume.

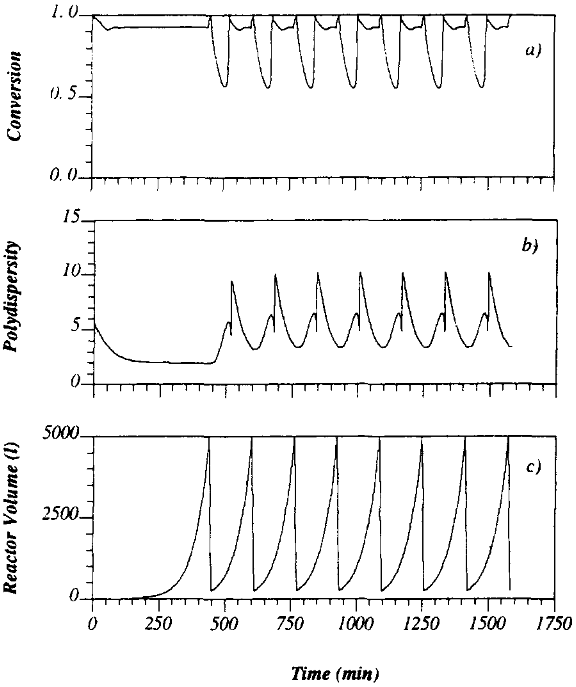

Figure 15. Dynamics of sequential semibatch operation.

$I_f = 0.06$ mol/L, $\hat{\theta} = 50$ min, minimum holdup 5%, discharge ratio $\gamma = 0.2$. (a) Conversion; (b) polydispersity; (c) reactor volume.

the reactor will be to complete conversion at the end of that stage. When inflow is resumed, the reactor is partially filled with the holdup volume left from the previous cycle; since this contains very little monomer it acts as a diluting solvent for the incoming feed, thus reducing the rate of polymerization and resulting in the initial drop in the conversion. After some time into the cycle, enough monomer forms for the polymerization rate to become appreciable again and the conversion rises. It becomes clear then that a small holdup volume is more desirable to minimize the dilution effect, unless a fast withdrawal rate is used and the monomer concentration in the reactor is not considerably decreased after the emptying phase.

Now that the usefulness of this scenario of operation in improving the quality of polymer obtained in semibatch reactors has been established, it is important to analyze its implications on the dynamics of such operation. As expected, operation under conditions emulating a continuous reactor might entail dynamic complexities of the oscillatory type. It was demonstrated above that when the suggested forcing cycle was applied to a reactor normally operating at a stable steady state, the resulting dynamics were periodic. If, however, the unforced reactor dynamics were periodic, forcing can result in one of three possibilities: quasiperiodicity, periodic phase locking, or aperiodic oscillations. This was demonstrated for example by Mankin and Hudson (1984) and Kevrekidis et al. (1986) for the forced CSTR, and by Kubíčková et al. (1987) for a fed-batch reactor. This last example particularly bears strong similarity to the case studied here. Figures 16–19 present an analysis of the behavior resulting when the limit cycle of Figure 6 is subject to the repeated filling/emptying forcing cycle. It is obvious from these figures that a strange attractor is observed; the oscillations are clearly aperiodic but bounded. Interest in this type of behavior for this particular class of reactors might be purely academic, yet it is not devoid of importance since operation under such conditions, even for a few cycles, will result in unexplainable fluctuations and extremely poor quality control. To study this behavior, however, one cannot limit the simulations to just a few cycles, since the mere observation of

Table 4. Effect of Minimum Reactor Holdup on Polymer Properties*

Cycle No.	Molecular Weight 5%	Molecular Weight 10%	Molecular Weight 20%	Polydispersity 5%	Polydispersity 10%	Polydispersity 20%
2	12,100	12,877	14,449	2.1384	2.2846	2.5917
3	12,158	13,032	14,653	2.1487	2.3112	2.6169
4	12,161	13,046	14,755	2.1492	2.3237	2.6361
5	12,161	13.047	14,764	2.1493	2.3140	2.6375
6	12,161	13,048	14,768	2.1493	2.3140	2.6382

*Discharge ratio $\gamma = 0.1$.

Table 5. Effect of Discharge Ratio γ on Polymer Properties. Minimum Holdup Volume = 5%

Cycle No.	Molecular Weight 0.1	Molecular Weight 0.2	Molecular Weight 0.3	Polydispersity 0.1	Polydispersity 0.2	Polydispersity 0.3
2	12,100	17,958	24,944	2.1384	3.2882	4.8535
3	12,158	18,690	26,783	2.1487	3.4289	5.2460
4	12,161	18,803	26,897	2.1492	3.4514	5.2690
5	12,161	18,824	26,903	2.1493	3.4557	5.2703
6	12,161	18,828	26,904	2.1493	3.4566	5.2703

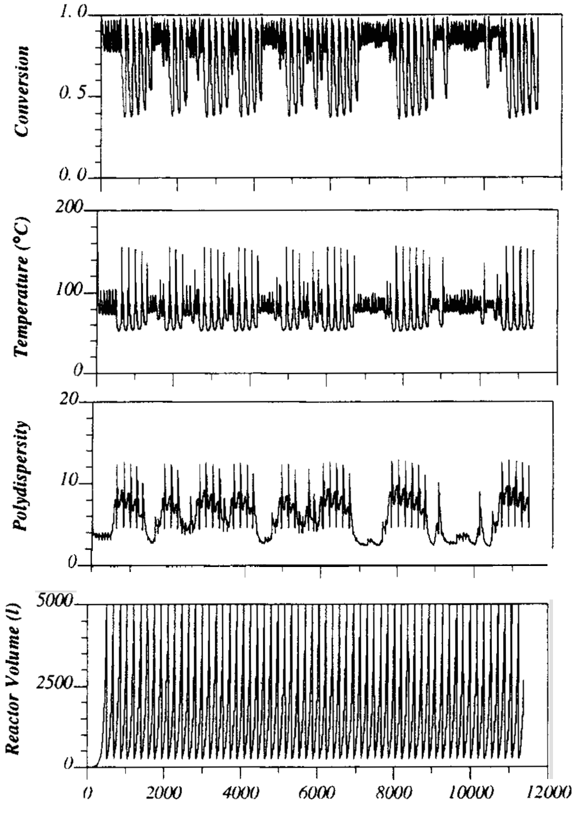

Figure 16. Dynamics of sequential semibatch operation exhibiting chaotic behavior.

$I_f = 0.04$ mol/L, $\theta = 57$ min, minimum holdup 5%, discharge ratio $\gamma = 0.1$. (a) Conversion; (b) temperature; (c) polydispersity; (d) reactor volume.

aperiodicity requires integration up to very long times. In Figure 16 one notices that not only is the behavior chaotic, but also that the fluctuations in the reactor states are very large. The polymer polydispersity repeatedly reaches values as high as 12.0, and rarely decreases to the vicinity of the desired value of 2.0. The structure of the resulting strange attractor is best viewed in the phase plane as in Figure 17 which demonstrates its chaotic nature. A more definite proof is presented, however, in Figure 18, which represents a stroboscopic Poincaré section of the strange attractor. In this figure, the values of temperature and monomer conversion are recorded at the end of each cycle; if the behavior were periodic, the number of points plotted would have to be finite and correspond to the order of periodicity of the attractor. Figure 18 clearly tends to show an infinite number of points indicating nonrecurrent behavior. Furthermore, the structure of this Poincaré section reflects a high degree of complexity as compared to those of famous chaotic attractors, indicating a possible higher degree of complexity. Quantitative characterization of the attractor is always necessary before one can classify it as either chaotic or not, however, this was deemed to be beyond the scope of this study; for now, it suffices to demonstrate the complex structure of the attractor. Finally, Figure 19 presents a strobscopic histogram of the monomer conversion at the end of each cycle, which is seen to fluctuate widely from one cycle to the next. It was argued earlier that

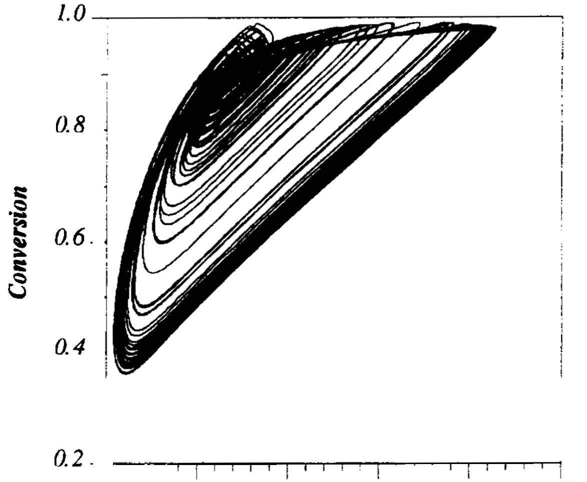

Figure 17. Phase plane illustrating the strange attractor of Figure 16.

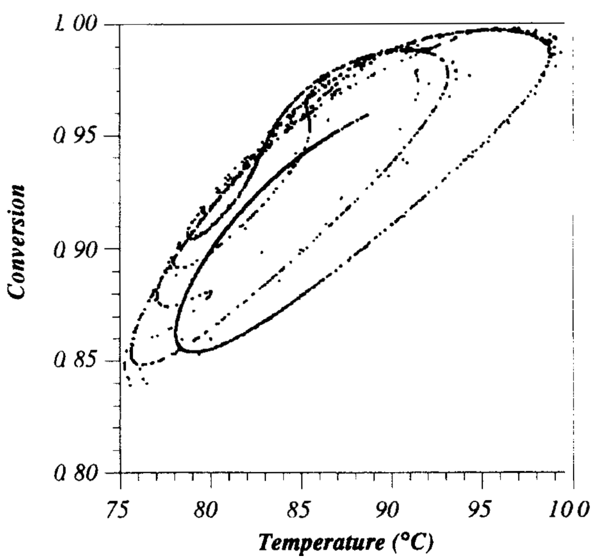

Figure 18. Stroboscopic Poincaré section of the strange attractor of Figure 16.

Points plotted are sampled at the end of each forcing cycle.

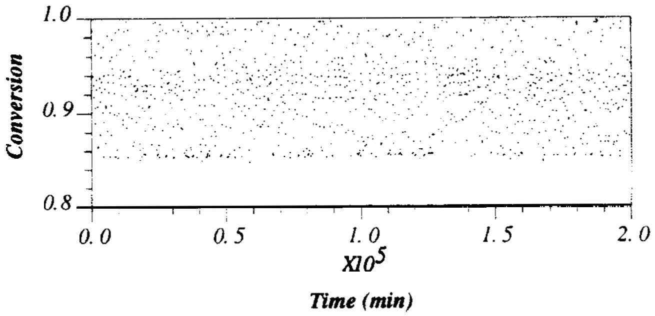

Figure 19. Stroboscopic histogram for the strange attractor of Figure 16.

Points represent monomer conversion at the end of each forcing cycle; other states and polymer properties exhibit similar behavior.

intracycle transient deviations could be tolerated if the reactor could reach a steady state some time during the cycle and thus yield polymer of consistent and desirable quality at the end of that cycle; clearly, this is not the case under this chaotic mode of operation.

It might seem unusual that while all the variables in Figure 16 exhibit chaotic behavior, the reactor volume is behaving in what appears as a perfectly periodic manner. In reality, it is not, and its appearance is only a result of the choice of the operational control policy for reactor filling and emptying. While it was possible to preset the time of each stage and allow the reactor volume to evolve in the same manner as all the other variables, I chose to use the maximum and minimum values of the volume as switching criteria. As a result, the reactor volume will perfectly oscillate between these two values, but the cycle time will fluctuate chaotically. This feature can hardly be observed in Figure 16, but it can be confirmed by a study of the simulation data. This approach to a switching policy was selected since it is easier and safer to implement, and should not have any considerable contribution to the behavior observed.

It was also found that chaos for the system at hand is not only obtainable when the underlying steady state is periodic, but that transition from a stable steady state in the unforced mode to chaos under forcing is also a possibility. This kind of transition, although previously reported in the literature for other systems (Cordonier et al., 1990), is a much rarer occurrence than the converse. This is demonstrated in Figure 20 where chaotic oscillations are obtained at a residence time shorter than that used in Figure 16. These conditions fall beyond the Hopf bifurcation point at which the limit cycle of this figure had emerged. Observation of the first cycle shows that the conditions are such that a stable steady state exists. The type of chaotic behavior obtained seems however to reflect a lower degree of complexity as evidenced from the stroboscopic Poincaré section of Figure 21 which is simpler in appearance and structure than Figure 18. This difference might be a result of the simpler nature of the unforced state of the attractor, however, it raises the question of whether this behavior is to be expected in general for periodically forced systems or whether it is unique to this case.

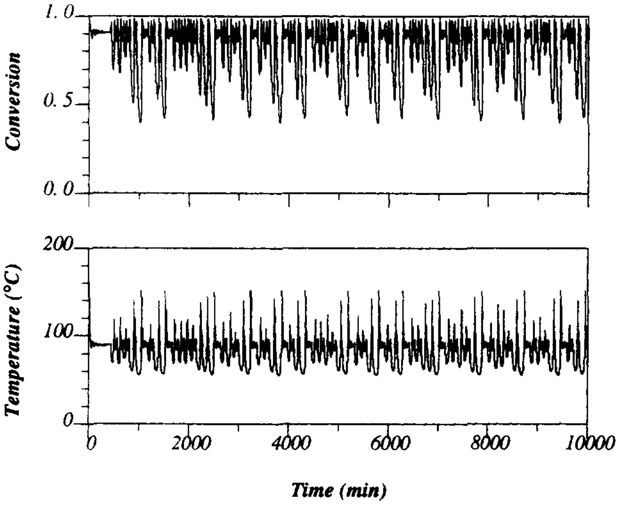

Figure 20. Dynamics of sequential semibatch operation exhibiting chaotic behavior.

$I_f = 0.04$ mol/L, $\hat{\theta} = 50$ min, minimum holdup 10%, discharge ratio $\gamma = 0.1$. (a) Conversion; (b) temperature. Observation of the first cycle shows that the underlying attractor for the unforced reactor is a stable steady state.

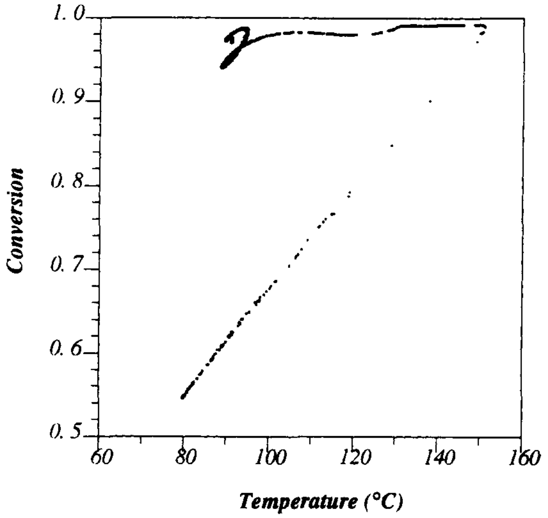

Figure 21. Stroboscopic Poincaré section of the strange attractor of Figure 20.

Points plotted are sampled at the end of each forcing cycle. Structure of this map is obviously simpler than that of Figure 18.

The analysis presented above has concentrated on demonstrating the possibility of chaos for the sequential semibatch operation, and on studying its effect on reactor operation and polymer properties, but did not address the mechanism of appearance of chaos or of its evolution. Sample simulations for the case of Figure 20 at different values of the minimum reactor holdup have yielded periodic solutions of various periodicity besides chaotic ones. Figure 22 presents orbits of periodicities one (P1), two (P2), four (P4) and chaos (P∞) indicating that period doubling might be the mechanism of transition to chaos in this system. It has to be mentioned, however, that these orbits do not necessarily represent the main period doubling cascade leading to the strange attractor of Figure 20, since their bifurcations were not followed rigorously using continuation techniques.

Practical Considerations

The analysis presented above is based on the assumption of an ideal reactor model. In practice, two major problems have to be dealt with: First, heat transfer to the cooling jacket might not follow the assumptions made earlier, especially at low reactor volumes. The effect of this nonideality can however be tolerated since it diminishes as the reactor fills up. Second, and more important, is the issue of mixing, which can be extremely difficult at small volumes since most reactors are designed to be used at least partially full. Poor mixing at the beginning of each cycle can result in severe heterogeneities in the molecular weight distribution that can outweigh the benefits resulting from the suggested operation mode. This can be alleviated by using a large minimum holdup, or by redesigning the agitation apparatus.

In the second part of this study (Chylla et al., 1996), these items will be discussed in more detail in the light of experi-

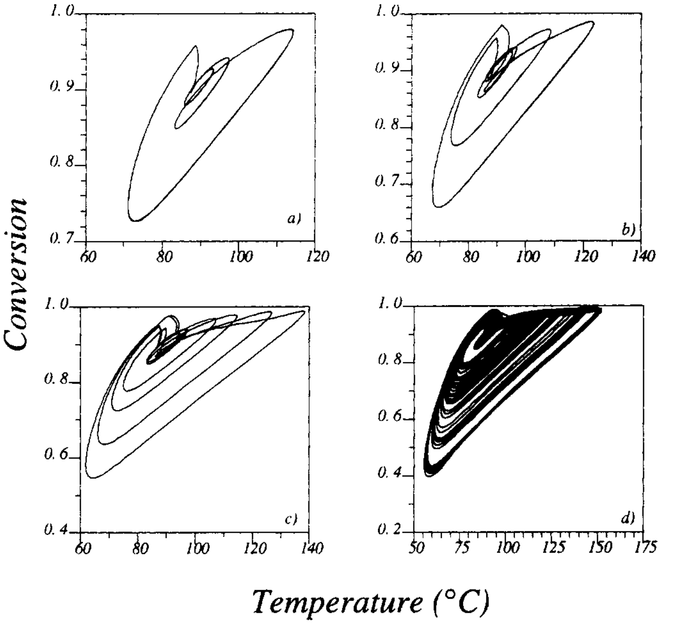

Figure 22. Effect of minimum holdup on the structure of the attractor in the conversion vs. temperature phase plane.

$I_f = 0.04$ mol/L, $\hat{\theta} = 50$ min, discharge ratio $\gamma = 0.1$. (a) P1 at 2% min holdup; (b) P2 at 4%; (c) P4 at 7%; (d) chaos at 10%.

mental pilot-plant results for the cases of single-batch and sequential semibatch operation.

Conclusions

It was demonstrated in this study that semibatch reactors can be operated using a strategy that allows the intensive states to reach equilibrium. This strategy was proven to be very useful for efficient CSTR startup, sequential semibatch operation, as well as for single semibatch operation. The suggested protocol, however, exhibits the same dynamic behavior as the CSTR analyzed by Teymour and Ray (1992b), and inherits all of its stability problems. It can exhibit steady-state multiplicity, limit cycle dynamics, as well as more complex periodic behavior. The behavior located is found to agree with the predictions of an earlier study of a different polymer system (Crowl, 1987), which reported experimental observations of such phenomena in pilot-plant reactors. It was also found that in sequential semibatch operation, the effect of the forcing cycle consisting of repetitive filling and emptying of the reactor can result in either periodic or chaotic oscillations. Under conditions yielding periodic operation, it was shown that consistent and desirable polymer quality could be obtained from each cycle.

It is important to notice that, although the analysis presented only considers the case of homopolymerization, it is easily extensible to copolymerization reactors. It is deemed even more important for those, since the copolymer composition highly affects the properties of the final polymer and hence should be controlled within tight limits.

Acknowledgments

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Notation

c_p = heat capacity of reaction mixture, cal/g·°C
f = initiator dissociation efficiency
$-\Delta H_R$ = heat of polymerization, cal/mol
k_d = rate constant for initiator decomposition, s^{-1}
k_p = rate constant for propagation, L/mol·s
k_t = rate constant for termination, L/mol·s
k_{trm} = rate constant for chain transfer to monomer, L/mol·s
P = live radical concentration, mol/L
q_{in} = inlet volumetric flow rate, L/min
q_{out} = outlet volumetric flow rate, L/min
t = time, min
T_c = coolant temperature, K
y = dimensionless temperature
y_{ref} = dimensionless reference temperature
z_i = dimensionless initiator concentration
τ = dimensionless time ($\tau = t/\hat{\theta}$)
φ_s = volume fraction of solvent in the feed

Literature Cited

Canu, P., S. Canegallo, M. Morbidelli, and G. Storti, "Composition Control in Emulsion Copolymerization: I. Optimal Monomer Feed Policies," *J. Appl. Poly. Sci.*, **54**, 1899 (1994).

Canegallo, S., P. Canu, M. Morbidelli, and G. Storti, "Composition Control in Emulsion Copolymerization: II. Application to Binary and Ternary Systems," *J. Appl. Poly. Sci.*, **54**, 1919 (1994).

Chylla, R. W., J. D. Campbell, and F. Teymour, "Dynamics of Semi-Batch Polymerization Reactors: II. Pilot-Plant Study," *AIChE J.*, **43**, 157 (1997).

Cordonier, G. A., L. D. Schmidt, and R. Aris, "Forced Oscillations of Chemical Reactors with Multiple Steady States," *Chem. Eng. Sci.*, **45**, 1659 (1990).

Crowl, D., "A Steady State, Stability and Dynamic Analysis of a Polymer Reactor," AIChE Meeting, New York (1987).

Hamielec, A. E., and J. F. MacGregor, "Modelling Copolymerizations—Control of Chain Microstructure, Long Chain Branching, Crosslinking and Molecular Weight Distributions," *Proc. Int. Berlin Workshop on Polymer Reaction Eng.*, K. H. Reichert and W. Geisler, eds., Hanser Publishers, New York (1983).

Kevrekidis, I. G., R. Aris, and L. D. Schmidt, "The Stirred Tank Forced," *Chem. Eng. Sci.*, **41**, 1549 (1986).

Kubíčková Z., M. Kubíček, and M. Marek, "Fed-Batch Operation of Stirred Reactors," *Chem. Eng. Sci.*, **42**, 327 (1987).

Mankin, J. C., and J. L. Hudson, "Oscillatory and Chaotic Behaviour of a Forced Exothermic Chemical Reaction," *Chem. Eng. Sci.*, **39**, 1807 (1984).

Nauman, E. B., "Maintenance of Product Quality During Transients in Stirred Tank Reactors," *Chem. Eng. Sci.*, **25**, 1595 (1970).

Teymour, F., "The Dynamic Behavior of Free Radical Polymerization Reactions in a Continuous Stirred Tank Reactor," PhD Thesis, Univ. of Wisconsin-Madison (1989).

Teymour, F., and W. H. Ray, "The Dynamic Behavior of Continuous Polymerization Reactors: V. Experimental Investigation of Limit Cycle Behavior for Vinyl Acetate Polymerization," *Chem. Eng. Sci.*, **47**, 4121 (1992a).

Teymour, F., and W. H. Ray, "The Dynamic Behavior of Continuous Polymerization Reactors: VI. Complex Dynamics in Full Scale Reactors," *Chem. Eng. Sci.*, **47**, 4133 (1992b).

Teymour, F., and W. H. Ray, "Chaos, Intermittency and Hysteresis in the Dynamic Model of a Polymerization Reactor," *Chaos, Solitions and Fractals*, **1**, 295 (1991).

Teymour, F., and W. H. Ray, "The Dynamic Behavior of Continuous Solution Polymerization Reactors: IV. Stability and Bifurcation Analysis," *Chem. Eng. Sci.*, **44**, 1967 (1989a).

Teymour, F., and W. H. Ray, "Improved Operation of a Semi-Batch Polymerization Reactor using Flow Rate Scheduling," AIChE Meeting, San Francisco (1989b).

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