Dynamics of Semibatch Polymerization Reactors: II. Pilot-Plant Study

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A semibatch flow scheduling strategy proposed by Teymour and Ray (1989, 1996) is evaluated for a polymerization reaction conducted in a pilot-plant reactor. The reaction used is the free radical terpolymerization of styrene, α-methyl styrene, and acrylic acid monomers initiated by an organic peroxide initiator and carried out in the presence of a reactive glycol ether solvent. This strategy was tested in both single batch and sequential semibatch modes. The process was shown to produce polymer of constant molecular weight properties and composition as inferred from acid number and monomer conversion measurements. This process could be used for obtaining polymer products from a semibatch reactor that are of comparable quality to CSTR products. Results indicate success of this process at meeting this objective; however, practical considerations relating to agitation and temperature control need to be properly addressed to ensure this success.

Introduction

Free radical addition polymerization reactions are usually carried out in stirred tank reactors. It has been shown for polymerization systems not dominated by branching reactions (Schork et al., 1993) that the narrowest molecular weight distribution and compositional distribution are obtained when the reactor behaves like a homogeneous continuous stirred tank reactor (HCSTR). The constancy of the reaction environment dominates over the distribution of residence times in the reactor. This is due to the fact that the average lifetime of a single polymer chain is far less than the average residence time in the reactor. For copolymerization, the constant concentrations of the comonomers ensures that the instantaneous polymer composition remains constant. Any deviations in the polymer reactor composition with respect to time (semibatch reactors) or spatial position (segregated CSTR) serve to broaden the molecular weight distribution and the compositional distribution.

Often, however, specialty polymers are produced in semibatch stirred tank reactors. In terms of operational considerations, the semibatch process is well suited to low volume products that are often produced in numerous grades. Economics associated with the waste of material during the startup and shutdown phases of a continuous process often dictate minimum run lengths which are much larger than short-term product demand. Therefore, semibatch reactors are favored for these applications despite the less homogeneous product they produce and their greater batch-to-batch variability.

Ideally for small volume polymer products, one would like the constancy in reaction environment of the HCSTR and the flexibility of the semibatch stirred tank reactor. In the first part of this series, Teymour (1996) analyzes the dynamics of semibatch reactors operated according to the flow rate schedule proposed earlier by Teymour and Ray (1989). His analysis shows that it is possible to schedule the feed flow rate of a semibatch reactor such that the intensive states of the reactor can be made to reach steady state, but that complex dynamic phenomena can also result depending on the choice of the reactor conditions and parameters. Refer to Teymour (1996) for a complete treatment of the derivation and dynamic analysis of the application flow schedule to a semibatch reactor.

This article describes an experimental pilot-plant study that evaluates the semibatch flow scheduling (SBFS) technique as

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applied to the free radical copolymerization of styrene and acrylic comonomers. The article discusses the practical implementation of the flow scheduling algorithm and the various startup scenarios that were investigated using dynamic simulation, the use of on-line energy balances to monitor the reaction progress throughout the batch, and the investigation of agitation and heat-transfer requirements and limitations.

Experimental System

Reaction mechanism

The experimental reaction used in this study is the free radical terpolymerization of styrene, α-methyl styrene, and acrylic acid monomers in the presence of a reactive glycol ether solvent. Polymerization is initiated by an organic peroxide initiator. The reactor mechanism is depicted below

Initiation

$$I \xrightarrow{k_d} 2R^{\cdot}$$

$$R^{\cdot} + M_{i,1} \xrightarrow{k_i} P_{i,1}$$

Propagation

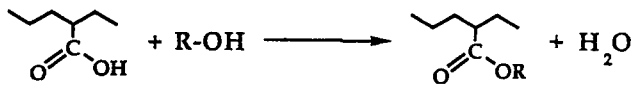
$$P_{i,n} + M_{j,1} \xrightarrow{k_{P_{ij}}} P_{j,n+1}$$

Termination

$$P_{i,n} + P_{j,m} \xrightarrow{k_{td_{ij}}} M_n + M_m$$

$$P_{i,n} + P_{j,m} \xrightarrow{k_{tc_{ij}}} M_{n+m}$$

Additionally, a condensation reaction between the hydroxyl-functional (R-OH) solvent and the carboxylic acid groups on the acrylic acid monomer or on polymer chains can take place



Experimental apparatus

In a typical semibatch process, all of the process solvent is precharged to the reactor and heated to reaction temperature. The monomers and initiator are fed at a constant rate over a fixed feed period. Finally, a hold period is often used to achieve high conversion.

In a continuous process, however, the solvent, monomer, and initiator are all fed into the reactor at a constant rate to maintain the desired residence time. In the SBFS process, the monomers, solvent, and initiator are all fed together like the continuous process, however, the instantaneous feed rate is determined by the volume in the reactor (Teymour, 1996).

The experimental system used is shown in Figure 1. $T_{j,\text{in}}$ is the temperature of the jacket inlet, and $T_{j,\text{out}}$ is the temperature of the jacket outlet. A pilot-plant scale jacketed stainless steel reactor was used for these studies. The reactor was equipped with a reflux condenser and a variable speed agitator (0–350 rpm). Heating and cooling in the reactor jacket were accomplished using recirculated heat-transfer oil. Monomer, solvent, and initiator were fed from an agitated feed tank mounted on a weigh cell. The feed mixture was pumped at the desired rate by a variable speed metering pump through a mass flowmeter to the reactor. The reactor was

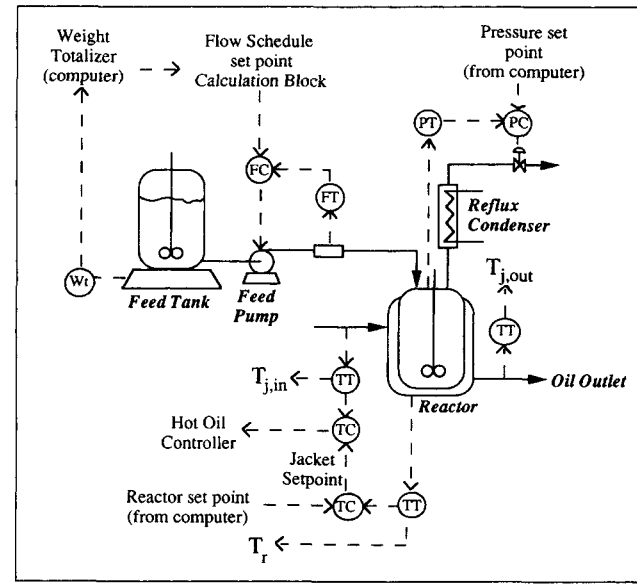


Figure 1. Experimental pilot-plant system.

equipped with a sampling valve through which reactor syrup samples were taken at various intervals throughout the batch. Once the batch was complete, a polymer gear pump was used to send the polymer melt to a vertical wiped-film evaporator where the unreacted monomer and solvent were stripped from the polymer. The high solids polymer melts were then applied to a water-cooled rotary drum flaker and converted to a solid flake form. The entire experimental pilot plant was monitored and controlled by a real-time process control system running on a standard personal computer equipped with a 80286 microprocessor.

Polymer syrup (reaction mixture as sampled directly from the reactor) and flake (dried polymer product) samples were analyzed for molecular weight using gel permeation chromatography and for free acid groups on the polymer chain by titration. This leads to the calculation of the acid number for the polymer which quantifies the fraction of polymer units attached to free acid groups, an important product performance quantity. In this article only normalized values of this variable are presented with a value of 1.0 representing the target acid number. It should be realized that in this system, two independent mechanisms control the acid number: (1) incorporation of acid monomer into the polymer, and (2) condensation of solvent and acid groups, on both the polymer backbone and acid monomer. Therefore, the acid number is not a measure of acid monomer composition in the chain. Nonetheless, one may infer the dynamics of the free acid composition by examining the polymer acid number over time. The molecular weight and acid number measurements were used to infer the homogeneity of the polymer molecular weight and composition over the course of a batch.

Theoretical Background

As reported by Teymour (1996), the intensive states in the semibatch reactor can be made to reach the equivalent CSTR steady state if its volumetric feed flow rate q (L/min) is varied proportional to the volume of the reactor contents, that is

$$q = \frac{V}{\hat{\theta}} \tag{1}$$

where $\hat{\theta}$ is the characteristic time constant (min), equal to the residence time of the equivalent CSTR process. If the density of the reaction mixture is assumed constant, a total mass balance on the semibatch reactor yields

$$\frac{dV}{dt} = q \tag{2}$$

Therefore, integration of Eq. 2 after substitution of Eq. 1 yields

$$q = \frac{V_i}{\hat{\theta}} \exp\left(\frac{t}{\hat{\theta}}\right) \tag{3}$$

V_i is the initial reactor volume (L). Equation 3 could be implemented directly, however, in practice flow disturbances introduce uncertainties in the reactor volume, resulting in cumulative error in its implementation. Alternatively, Eq. 1 can be used when expressed as

$$q = \frac{V}{\hat{\theta}} = \frac{1}{\hat{\theta}} \int dV \tag{4}$$

Finally, since mass and mass-flow rates are more commonly measured in a plant environment than volumetric flows, the mass equivalent of Eq. 4 was actually implemented in this study. This is obtained by multiplying both sides of the equation by the density of the reaction mixture

$$\dot{m} = \frac{1}{\hat{\theta}} \int dm \tag{5}$$

As noted, this method assumes a constant density for the reaction mixture that is equal to the density of the monomer feed. Normally, polymerization leads to a volume shrinkage and thus results in a higher density at higher conversion, but it was shown by Teymour (1996) that this shrinkage has a negligible effect on reactor dynamics. The calculation of total mass by integration was deemed adequate for the purpose of this study.

Whether Eq. 4 or 5 is used, one is faced with an inherent problem in the formulation. It is obvious by inspection that a singularity in the flow schedule exists at the start of the batch. A nonzero flow cannot be obtained unless an initial amount of material is present in the reactor. One could, of course, get around this problem by priming the reactor with a small initial charge, but then two concerns arise: How much material should be in the reactor initially? What should it be composed of? Theoretically, the initial volume is best calculated by run time requirements; in practice, however, the minimum initial volume is determined by the minimum amount of material that can be agitated in the vessel, which represents about 10–15% of the total reactor volume for our experimental pilot-plant reactor.

Unfortunately, the issue of the composition of the initial charge is not quite so straightforward. Theoretically, to maintain a constant composition in the reactor at all times, the initial charge should be composed of all reactor components (monomer, solvent, initiator, and polymer) at their steady-state concentrations. This, however, is not a practical solution since it is not possible to hold the steady-state concentrations at reaction temperature without reaction occurring. Therefore, a number of possible startup scenarios have been screened using a dynamic simulation model of a polymerization reactor to assess the best options. The mathematical model used is a modified version of the model of Teymour (1996); it has the same basic structure but was modified to incorporate the specific reaction steps that are unique to the reaction mechanism at hand. In all simulations, a characteristic time $\hat{\theta}$ of 30 min was used since the goal is to match the equivalent CSTR residence time. Figures 2 and 3 show the acid number and molecular weight predictions for six potential startup scenarios and composition formulations for the initial reactor charge:

(1) Steady-state initial conditions (this case is not practically attainable, but was used as a point of reference).

(2) Polymer/Solvent mixture at the steady-state concentrations (same as 1 after omitting monomer and initiator).

(3) Nonreactive solvent.

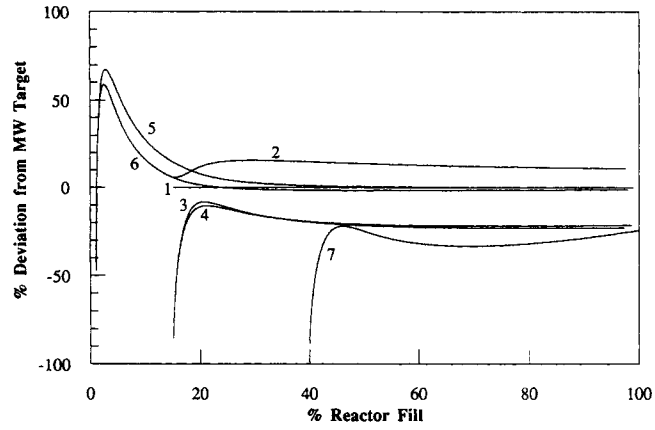


Figure 2. Weight-average molecular weight as predicted by simulation for the seven possible scenarios.

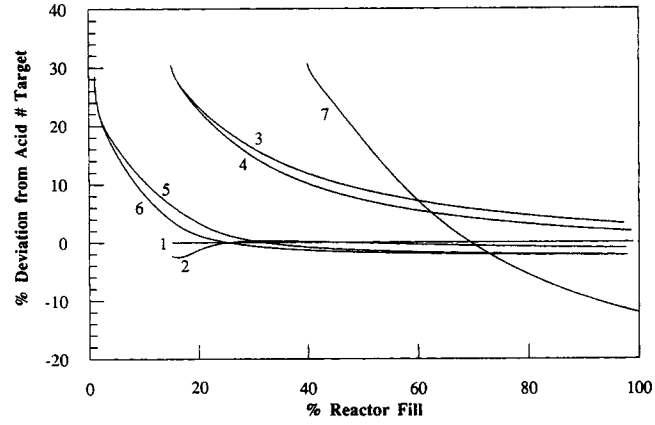


Figure 3. Acid number as predicted by simulation for the seven possible scenarios.

(4) Process solvent (reactive solvent).

(5) Empty reactor (a 15% initial charge is assumed for the flow schedule calculation).

(6) Same as case 5, but initially filled at a constant flow rate up to 15% full.

The case 6 scenario was introduced to compensate for the fact that the flow schedule trajectory in case 5 is based on an incorrect initial reactor volume. In case 6, the initial monomer feed flow rate calculated in case 5 is used to fill the reactor to 15% of its volume, then the flow schedule is turned on in a bumpless transfer mode without any discontinuous jumps.

In addition, these six scenarios are also compared to the standard semibatch process (case 7), in which all the solvent is loaded into the reactor and the monomers and initiator are fed over a two hour period followed by a hold period.

As seen in Figures 2–3, case 6 is the most successful at approximating a steady-state scenario in both the polymer acid number and molecular weight, while the standard semibatch procedure results in the highest deviation from the ideal CSTR behavior in both variables. This deviation is most exemplified by the continuous drop in acid number of the polymer for case 7 which is a result of the extended contact of the polymer with a high concentration of the reactive solvent. This behavior even extends into the hold period, during which a further decrease in acid number is observed. It should also be noted that in cases 5 and 6, a steady state is reached even before the reactor is filled to 20% of its volume, which will tend to minimize the impact of transient deviations from ideality on the quality of the final polymer produced. Since the startup method of case 6 seems successful and since it is one of the simplest to implement from an operational point of view, it was the only case tested experimentally.

Calorimetric Process Monitoring

The flow rate schedule proposed here is run in an open-loop mode, thus it is incapable of correcting for process upsets. A full-scale implementation of this protocol should include feedback or supervisory control, but in the absence of those an adequate monitoring technique has to be employed. In this study, on-line calorimetric monitoring has been used for the evaluation of each individual batch and for the estimation of the local reaction rates in each. Important implications of the heat-transfer modes observed in this analysis on process control operation were analyzed and will be discussed later.

In theory, the amount of heat transferred in this process should be constant and identical to that of the equivalent CSTR process, since concentrations of all reactants remain invariant throughout the process.

Energy balances can be derived for both reactor and jacket sides of the reactor illustrated in Figure 4. These are given by

Reactor Heat Balance

$$MC_p \frac{dT_r}{dt} = \sum_i F_{\text{in},i} C_{p,i} (T_{\text{in}} - T_r) + Q_r - Q_j \qquad (6)$$

Jacket Heat Balance

$$M_c C_{p,c} \frac{dT_c}{dt} = F_c C_{p,c} (T_{c,\text{in}} - T_c) + Q_j - Q_{\text{loss}} \qquad (7)$$

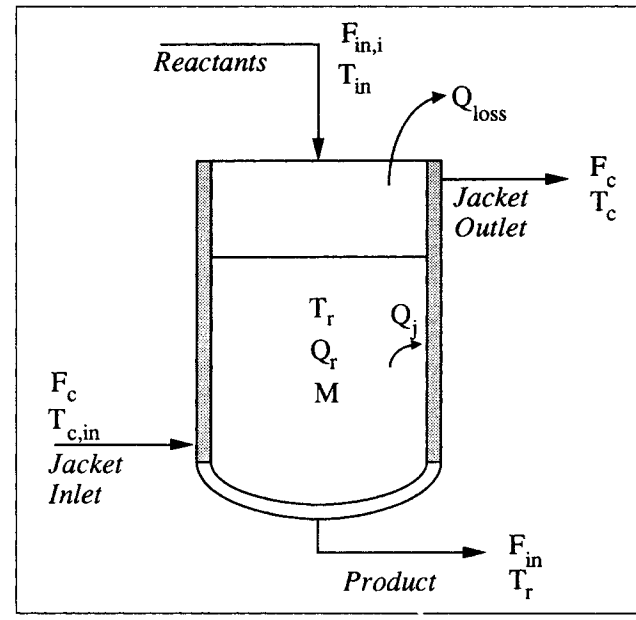


Figure 4. Energy balance notation.

Q_j is heat transferred to the jacket (kJ/kg/C). C_p is the heat capacity of reactor contents, $C_{p,c}$ is the heat capacity of jacket coolant, and $C_{p,i}$ is the heat capacity of component "i." Furthermore, Eqs. 6 and 7 can be combined to solve for the heat released by the reaction Q_r (kJ/kg/°C)

$$Q_r = MC_p \frac{dT_r}{dt} - \sum_i F_{\text{in},i} C_{p,i} (T_{\text{in}} - T_r) + M_c C_{p,c} \frac{dT_c}{dt} - F_c C_{p,c} (T_{c,\text{in}} - T_c) + Q_{\text{loss}} \qquad (8)$$

Equation 8 can be used for the on-line estimation of Q_r if the necessary measurements are taken. These include the total mass and temperature in the reactor (M, T_r), the flow rate and temperature of the feed (F_{in}, T_{in}), the jacket inlet and outlet temperatures ($T_{c,\text{in}}$, T_c), the mass of coolant in the jacket (M_c), and an estimate of the heat loss Q_{loss} (kJ/kg/C). In addition, the derivatives of the reactor and jacket temperatures can be numerically estimated on-line and each term in Eq. 8 can be estimated individually, allowing for added insight into the major sources of heat removal in the system.

In Eq. 8, the instantaneous heat generation due to reaction is expressed as a function of the energy accumulation terms in both the reactor and the jacket, the sensible heat increase of the feed, the sensible heat increase of the heat-transfer fluid circulating in the jacket, and the heat loss to the surroundings. When the process is at steady state, the two accumulation terms are zero, however, that is not the case in general. The major practical problem to overcome in solving the on-line energy balances is to avoid the propagation of measurement errors through the balance equations. In particular, accurate evaluation of the derivative terms in the presence of process and measurement noise is a major issue. This was achieved by using a high-order backward differentiation formula. Alternatively, a Kalman filter (Astrom and Witten-

Table 1. Heat Balance Physical Constants

ρ	1.0 kg/L
$C_p, C_{p,i}, C_{p,c}$	0.60 kcal/kg·°C
F_c	30.0 kg/min
M_c	3.60 kg
T_{in}	15.0°C

mark, 1984) could have been used, however, the differentiation technique was found adequate for this work and easier to implement on the process control software used in the experimental pilot plant.

The procedure used to develop expressions for the derivative estimates was taken from Gerald (1980). A third-order Newton-Gregory Backward polynomial was employed and resulted in the following derivative estimate

$$\frac{dT_k}{dt} = \frac{1}{h}(1.833T_k - 3.0T_{k-1} + 1.5T_{k-2} - 0.333T_{k-3}) \quad (9)$$

where the temperature derivative at time k is expressed as a linear combination of the current and three most recent temperatures and h is the sampling interval. The mass of the coolant fluid in the jacket was estimated from reactor geometry, and heat capacities were taken from literature. The circulation rate of the coolant was estimated from the orifice plate pressure drop, and the feed rate of monomer and solvent was measured directly using the mass flowmeters. Temperature measurements of the reactor contents, inlet and outlet coolant temperatures, and feed temperature completed the required information to estimate the instantaneous heat generation as given by Eq. 8. The physical constants used in the on-line heat balance are shown in Table 1.

Results and Discussion

The flow schedule selected (case 6) was implemented experimentally in two different modes: namely single batch operation or consecutive semibatch operation. In the latter mode, the reactor is not fully emptied between batches, thus allowing for better control of the reactor dynamics as shown by Teymour (1996). It should be noted, however, that the simulations presented by Teymour were for an open-loop reactor, while in the experiments conducted here, attempt is made to control the reactor temperature via feedback control.

Single batch operation

For comparison purposes, the results of experiments using a standard semibatch process to synthesize the polymer are described. In the standard process, all of the process solvent was precharged to the reactor and preheated to the desired reaction temperature of 160°C. The monomer/initiator feed mixture was fed to the reactor at a constant rate chosen to result in a 2 h fill period, which was then followed by a 30 min hold period. Reactor syrup samples were collected at 60, 90, 120 and 150 min. In the SBFS process, the monomer/solvent/initiator feed mixture was fed to an empty preheated reactor at a constant flow rate calculated to fill 15% of the reactor volume in 30 min. After this point, the feed rate was recomputed every 30 s using Eq 5. This process

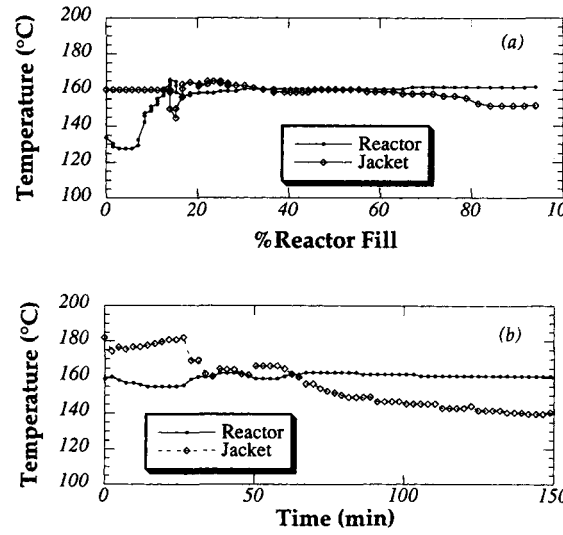


Figure 5. Reactor and jacket temperature dynamics for (a) the SBFS single batch process and (b) the standard process.

SBFS dynamics plotted against % reactor fill to illustrate that the temperature is steady after a level of 15% is reached. The standard reactor is filled at a constant feed rate up to 120 min, then held batchwise thereafter.

resulted in a total batch time of 99 min. It was necessary to agitate the reactor at 350 rpm to maintain a well-mixed condition in the reactor; agitation requirements are discussed in more detail later. Reactor syrup samples were taken from the reactor at 30, 50, 70 and 90 min.

The results of these two processes are compared in Figures 5–7. Figure 5 illustrates the dynamics of the reactor and jacket temperatures during the operation of both scenarios. It is clear that the feedback controller is successful in controlling the reactor temperature for both cases around the setpoint of 160°C. The only exception is during the heatup period of the SBFS reactor in which the jacket temperature was manually set to 160°C; it can be seen that a considerable amount of time is needed to overcome the cooling effect of the incoming feed stream. More discussion about the relative importance of different heat-transfer mechanisms is presented later. It is more important now to notice the main difference in the behavior of these two reactors: while the SBFS reactor temperature can be controlled by minor manipulations of the jacket temperature, the case is not so for the standard process. The jacket temperature needed to maintain a constant reactor temperature for the latter changes drastically over time, indicating that the rate of heat evolution due to reaction is variable and that the polymer produced there should have broader molecular weight and composition distributions. This is confirmed in Figures 6 and 7, which compare the molecular weight properties and acid numbers of the polymer produced by both processes. An additional SBFS run is shown in these figures to illustrate the level of reproducibility, however, this run is part of a consecutive set that will be discussed in the next section. Figure 6 shows that in both processes the weight-average molecular weight appears to be more or less steady during the course of each run. This is mainly a result of the strong dependence of the molecular weight on reactor temperature; the effect of changing con-

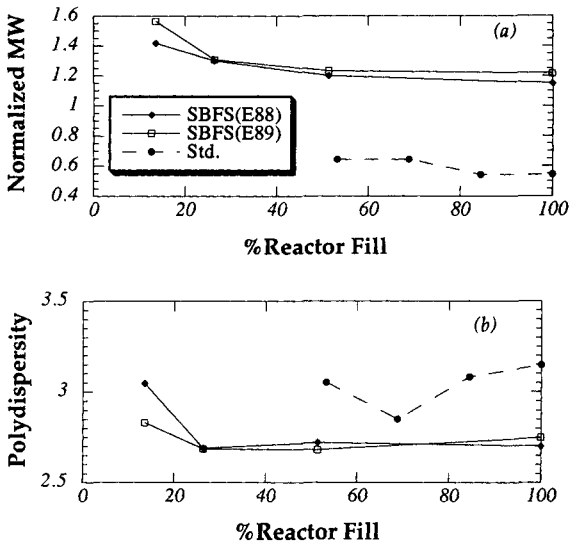


Figure 6. Weight-average molecular weight and polydispersity for SBFS (E88) and standard processes.

First cycle of a sequential semibatch run (E89) is added for comparison.

centrations and reaction environment is, however, evidenced in the standard process case by the higher polydispersity resulting at the end of the batch (3.2 as compared to 2.7). This rather broad polydispersity is indicative of polymer chains being formed under heterogeneous reaction environments. The polydispersity of the SBFS case was 2.7 as opposed to 2 for the ideal linear polymerization. This is caused by chain transfer to polymer branching that exists for this system. On the other hand, the normalized acid number can be seen to change dramatically throughout the course of the batch for the standard process (Figure 7), also indicative of a changing reaction environment. The same is somewhat true of the SBFS process, but is counteracted by the fact that this composition variable seems to stabilize by the time the reactor is approximately 40% full.

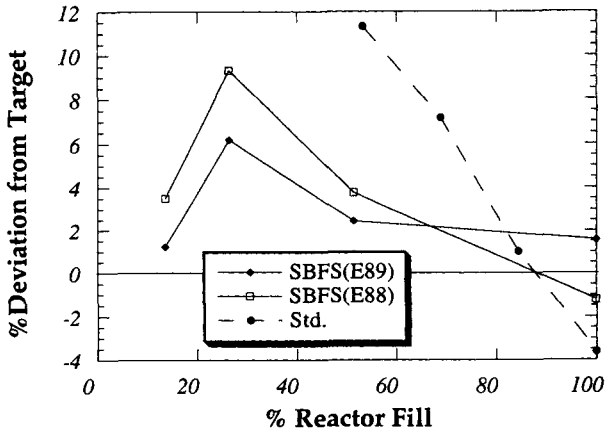


Figure 7. Acid number results for the SBFS (E88) and standard processes.

First cycle of a sequential semibatch run (E89) is added for comparison. Scale represents % deviation from targeted value.

The results of the SBFS process are somewhat satisfactory, but warrant additional efforts towards the improvement of polymer quality. The external process measurements suggest that a pseudo-steady state had been achieved, but the polymer quality measurements show deviations from their desired values. It was felt that these deviations from the ideal could have been due to the empty reactor startup and to the relative slowness of the condensation reaction, which has a strong effect on the polymer acid number. Therefore, subsequent experiments were conducted whereby a series of SBFS batches were run, using the heel of the previous batch to begin the following batch.

Sequential semibatch operation

In the multiple batch experiments, the first batch is identical to a single SBFS experiment. It is then followed by a 13 min constant rate emptying stage that drains the reactor contents down to 25%. Subsequent runs are operated between 25 and 100% full according to the appropriately calculated SBFS schedule. This results in a fill time of 42 min. A total of four filling and emptying cycles were used as shown by Figure 8, however, the last batch had to be cut short since the prepared feed mixture ran out prior to its completion.

As expected and as illustrated in Figure 8, the reactor dynamics are now periodic instead of steady. It is clear that the fill/empty forcing cycle that is imposed on the reactor causes the steady state achieved in the first cycle to bifurcate to oscillatory dynamics in subsequent cycles. This agrees perfectly

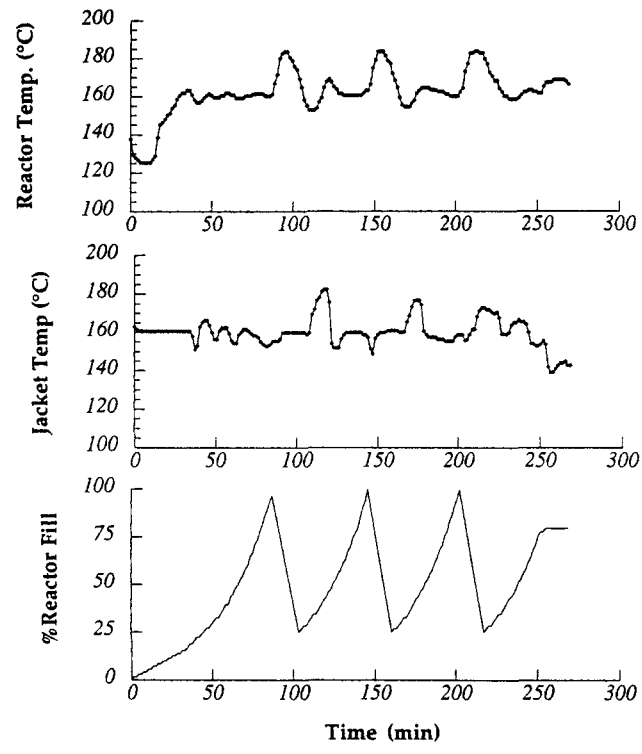


Figure 8. Reactor, jacket temperature, and reactor volume dynamics for a sequential semibatch experiment.

First cycle is filled at a constant rate up to 15%, then according to the flow schedule. Reactor is drained down to 25% before the start of each subsequent cycle.

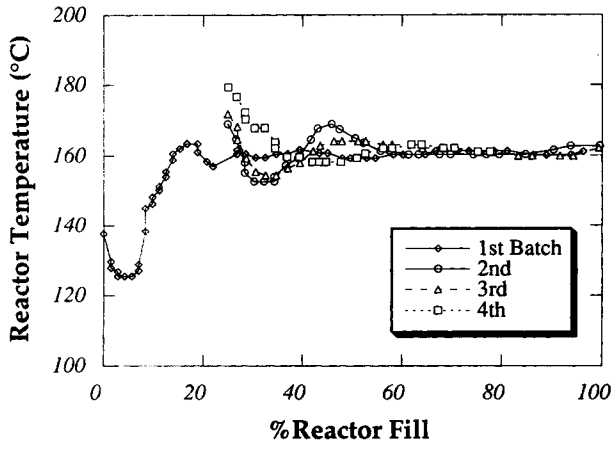


Figure 9. Temperature vs. % reactor fill for all four *filling* cycles of Figure 8.

with the simulation results presented in part I of this article (cf. Figure 12), despite the fact that feedback control was used here. It can be seen in Figure 8 that the reactor temperature starts rising as soon as the feed is stopped and the emptying stage is started. This stage effectively represents a batch hold period during which additional polymerization occurs, resulting in an increase in temperature (this is also related to the loss of the feed cooling effect as discussed later). As soon as the next cycle is started and fresh feed is introduced, the reactor temperature starts dropping and then oscillates until it stabilizes later in the cycle. It should be emphasized, however, that these large deviations in reactor temperature occur at relatively small reactor volumes and hence their effect on polymer properties is minimized. Figure 9 presents the temperature profiles vs. reactor volume for all four consecutive filling cycles, and confirms that the reactor temperature deviations disappear before the reactor is half-full.

Monomer conversions are found to reach a steady state by the end of the first batch and to remain relatively unaffected by the periodic dynamics thereafter, as shown in Figure 10. This indicates that a high degree of polymer composition homogeneity is to be expected in the product. An observation that could be confirmed by the acid number measurements

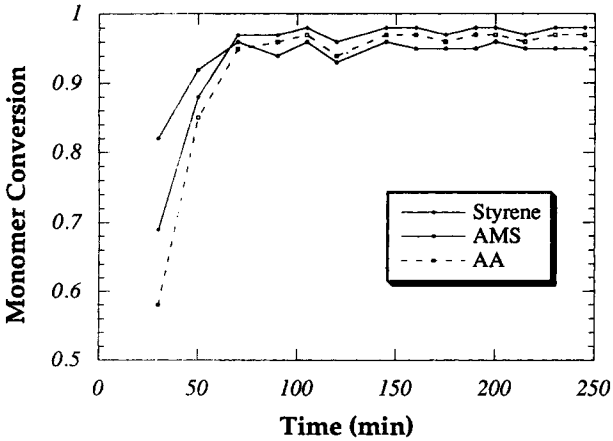


Figure 10. Monomer conversion dynamics for the sequential semibatch experiment of Figure 8.

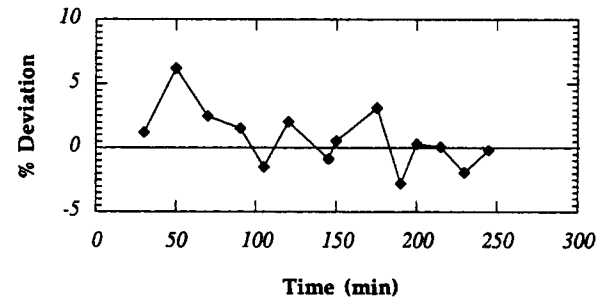


Figure 11. Acid number dynamics (as % deviation from target value) for the sequential semibatch experiment of Figure 8.

presented in Figure 11 shows that the polymer acid number remains within $\pm 3\%$ of its desired value after the first cycle. More importantly, one should notice that these limits are obeyed throughout the batch and not only at the end, indicating better composition homogeneity than that obtained in the standard process which can be made to yield satisfactory acid number averages (Figure 7). As shown in Figure 7, the acid number of the standard process steadily decreases in time from the start of the batch to the end, indicating that the composition of the polymer was different at the beginning than at the end of the reaction, resulting in a much more heterogeneous polymer than is produced in either a continuous reactor or the SBFS process.

Figure 12 shows the molecular weight and polydispersity for the sequential semibatch process. As seen earlier for the SBFS process, the molecular weight at the end of the first cycle is approximately 20% higher than desired and the polydispersity is ~ 2.7. However, the molecular weight of the polymer produced in the second and subsequent cycles is at or near its desired value, and the polydispersity drops to $\sim$ 2.4. It is noteworthy that the temperature excursion observed at the end of each SBFS cycle did not adversely affect the molecular weight of the polymer produced. All of this con-

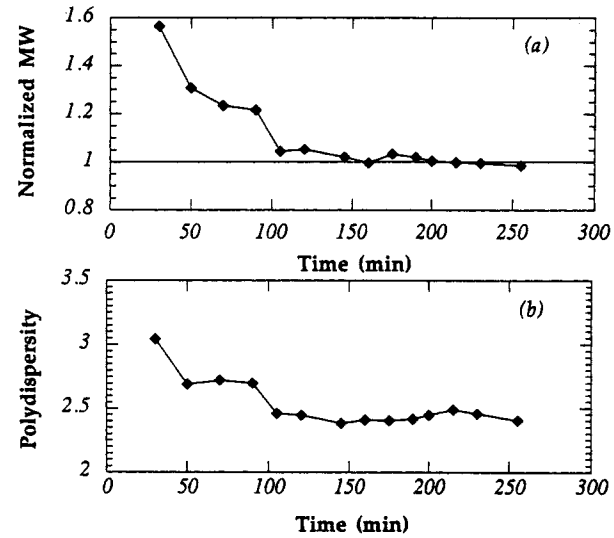


Figure 12. Molecular weight and polydispersity dynamics for the sequential semibatch experiment of Figure 8.

firms that the larger deviations in temperature, conversion and polymer properties observed in the first cycle of operation are a direct result of the necessity of using a modified feed strategy (constant feed followed by SBFS) to satisfy the agitation and heat-transfer requirements. It also shows that the sequential process should be selected whenever suitable for production volume requirements, since it results in improved performance.

It this study, we have limited our experimentation to a single set of parameters for the forcing cycle of reactor filling and emptying. Further fine-tuning and optimization of the process can be carried out by manipulating the reactor heel size and drainage time as illustrated by Teymour (1996). However, even the limited experimentation we have carried out has illustrated the success and usefulness of this process.

Agitation requirements

One of the key experimental findings in this work was that the reactor agitation requirements are key design criteria for successful implementation of the SBFS process. There were several experiments run prior to the ones reported here. These experiments were characterized by very poor temperature control and large oscillations in the instantaneous heat load. It appeared that the root of the problem was poor mixing, especially near the end of the batch where the flow rate was the highest. These early experiments were performed with the agitator operating at 105 rpm. This speed is sufficient to properly blend the incoming feed using a traditional 2 h feed period. The monomer feed was also introduced on top of the liquid surface in these experiments. It was not until the reactor agitator had been turned up to its highest speed (350 rpm) and the dip tube in the reactor placed subsurface near the impeller that the reactor temperature was controllable. In retrospect, this should have been obvious since the final flow rate of the flow schedule is equal to the flow of a continuous reactor of the same size, requiring high levels of agitation. With low levels of agitation and high flow rates at the end of the batch, the monomer tends to collect in pools in the reactor prior to being dispersed. This results in a local cold spot at the monomer addition point, which slows down the reaction in this zone. The reactor temperature then falls, further reducing the reaction rate. Meanwhile, the controller attempts to compensate for this drop by increasing the reactor jacket temperature. Eventually, the concentrated monomers become mixed, their concentration increases, and an accelerated reaction burst results. This periodic sequence of events results in uncontrollable reactor temperature. This behavior was evident in all batches made without adequate agitation. The reactor agitation system must be designed specifically for the flow rates involved in this process for successful implementation. These agitation requirements are identical to those of the equivalent CSTR process.

On-line calorimetry

Besides the obvious heat-transfer problems expected at low reactor levels, more important conclusions about the particulars of the heat-transfer process can be made from the observations presented here. From a practical point of view, the on-line heat balance was an invaluable aid to us during the

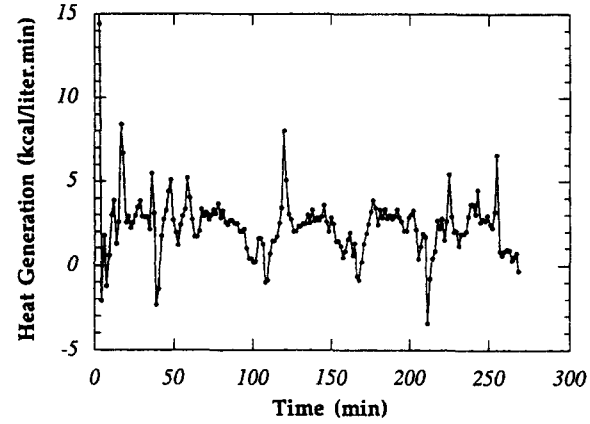


Figure 13. On-line calculation of heat generation rate for the sequential semibatch experiment of Figure 8.

experiments, supplementing our knowledge learned from process measurements alone. It assisted us in formulating our hypotheses on inadequate agitation and monomer segregation during the early stages of experimentation. This on-line heat balance, coupled with the process measurements, led us to understand the periodic sequence of events described above that results in temperature control problems. After equipment modifications were made to the agitation and feed setup, the SBFS experiments showed markedly different heat generation estimates. For example, the calorimetry results for the sequential process are presented in Figure 13, which shows that with the exception of very brief upsets in the heat generation during the emptying cycle, it remains essentially constant over the course of the batch, agreeing with the other process and quality data that suggest the reactor was operating at near-steady conditions. Through closer observation of Figure 13 one can conclude that the heat removal via sensible heating of the cold monomer feed is by far the largest source of heat removal, accounting for perhaps as much as 85–90% of the total heat removal. This is further confirmed when individual terms of the energy balance are computed from the on-line data collected. Calculation of the time-averaged values of these terms show that the sensible heat term is responsible for about 97% of the heat removal duty. However, the on-line calculation neglects the undermined reactor heat losses and uses a constant heat capacity for the sensible heat calculation. More rigorous off-line calculations result in the corrected estimates shown in Table 2, which still show sensible heating to be the dominant heat-transfer mechanism at 73% of the total duty. This somewhat surprising result is a critical conclusion; it suggests that the reactor temperature should be controlled by manipulating the monomer feed temperature, not the reactor jacket in which only 4% of the heat of polymerization is removed. This control scheme has the

Table 2. Corrected Heat Removal Breakdown

Heat Removal Term	kcal/L·min	%
Sensible heat	2.08	73
Heat losses	0.66	23
Heat transfer to jacket	0.11	4
	2.85	100

added advantage of having a significantly faster response time than jacket manipulation, which would make reactor temperature control much less variable. Further analysis indicated that the solvent contributes approximately 55% of the sensible heat of the feed, due to its higher heat capacity. In the standard semibatch process in which all of the solvent is loaded initially into the reactor, a significant amount of the sensible heat of the feed is lost, and the ability to adequately control the reactor temperature decreases.

As pointed out earlier in discussing Figure 8, it is this strong dependence of the cooling mechanism on the sensible heat requirements of the incoming feed stream that results in large thermal upsets when that is interrupted. The large temperature spikes observed in Figure 8 at the beginning of each drainage cycle could be minimized if some secondary means of cooling were made available. This could effectively improve the performance of the sequential operation mode and result in better control of the polymer properties.

Conclusions

The semibatch flow schedule process (SBFS) was tested experimentally using a free radical solution polymerization as the model system to evaluate its potential to imitate CSTR behavior. Adequate mixing in the reactor was shown to be of major importance for successful operation of this process, due to the high monomer flow rates required at the end of the batch. If this criterion was met, the process was shown to produce polymer with a constant molecular weight and acid number throughout the batch. As compared to a standard semibatch process, the polymer composition as measured by acid number for the SBFS were shown to be less variant throughout the batch and the molecular weights had a lower polydispersity. This behavior was caused by the constant concentration profile throughout the SBFS process, as contrasted to the standard process in which the concentration of polymer, solvent, and monomer change as a function of batch time. The conversions of monomers and of the reactive solvent in the SBFS process were shown to be constant throughout the batch, indicating a constant concentration profile.

The reproducibility from batch to batch of the SBFS process was tested by running four consecutive batches. It was found that the acid number, molecular weight, and conversion of the first batch showed some variation, but settled to the constant steady-state levels in subsequent batches. The variation observed in the first batch was magnified by the use of a nonideal flow schedule to meet agitation requirements as possible. It is felt that this problem can be minimized by designing the agitation system to mix smaller volumes.

The analysis shows that the sequential SBFS process is successful in meeting the desired production criteria as predicted in part I of this article, but that additional practical considerations regarding heat transfer and agitation have to be taken into account. It should be understood that the SBFS process could not be recommended whenever continuous operation is a viable alternative, mainly because of its more complicated, batchwise operation. However, for processes where required production volumes do not yet make continuous processing economically attractive, or in instances where downstream processing equipment are not sized to handle the continuous high throughput of a CSTR, the selection of a SBFS process is well justified.

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Literature Cited

Astrom, K. J., and B. Wittenmark, *Computer Controlled Systems, Theory and Design*, Prentice-Hall, Englewood Cliffs, NJ (1984).

Gerald, C. F., *Applied Numerical Analysis: Second Edition*, Addison-Wesley, Reading, MA (1980).

Schork, F. J., P. B. Deshpande, and K. W. Lefew, *Control of Polymerization Reactors*, Marcel Dekker, New York (1993).

Teymour, F., "Dynamics of Semibatch Polymerization Reactors: I. Theoretical Analysis," *AIChE J.*, **43**, 145 (1997).

Teymour, F., and W. H. Ray, "Improved Operation of a Semibatch Polymerization Reactor Using Flow Rate Scheduling," AIChE Meeting, San Francisco (1989).

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