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Chemical Engineering Journal 70 (1998) 1–8

Chemical Engineering Journal

Control of batch suspension polymerization reactor

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Received 17 July 1996; revised 15 December 1996; accepted 1 December 1997

Abstract

The automation and control of polymerization reactors that operate in batches is quite a difficult task. The gel effect and the absence of a stable operational state are factors that determine the need for special control systems. In this study, a methodology is implemented for controlling the operation of a batch polymerization reactor, utilizing an adaptive controller of the type STC (Self Tuning Controller). By utilizing a model of the polymerization process, the necessary operational conditions were determined for producing the polymer within the desired characteristics. Variables of the mean molecular weight type and the polydispersion rate were utilized as polymer quality parameters. Experimental tests in a pilot unit of polystyrene production in suspension, showed the capacity of the STC for controlling this type of reactor. The results also showed that, from the methodology utilized for determining the operational variables, polymers with previously defined characteristics can be produced.

Keywords: Self-tuning controller; Batch polymerization reactor; Suspension polymerization

1. Introduction

In polymer industries, the automation and control of reactors that operate in batches lead to a more secure and stable operation, promoting gains in quality and productivity. Environmental factors, such as reduced generation of residues and decrease in energy consumption, are also to be considered.

The implementation of an automation and control system in these polymerization reactors, requires, in addition to suitable instrumentation, knowledge of the operational conditions that will produce the product with desired characteristics.

In the case of polymers, the quality of the product can be measured by means of the mean weighted molecular weight and the polydispersion rate.

In this way, the decision and actual operation of the batch process in order to achieve a pre-specified product should be seen as a two stage procedure: the first is related to the determination of reference values for control variables selected for the process, while the second stage concerns projecting and implementing a control system capable of maintaining the process, operating within the reference values obtained in the first stage.

For the polymerization of styrene, which was tested in this study, specialized literature and industrial practice have shown that by controlling the temperature of the reactor operation and of the initial concentration of the initiator, it is possible to obtain products with previously defined characteristics.

Many authors have studied this problem. Sacks et al. [1] and Wu et al. [2] utilized Pontryagin's maximum principle in the stage of determining reference values. Although efficient, this method shows great difficulty for application in processes in which the mathematical models that present some degree of complexity. In some cases, inappropriate, or even physically unfeasible, solutions can be obtained. Several other authors [3–16] present alternatives to the first stage of the procedure. However, only a few authors show an experimental validation for the results obtained. The great majority simply report computational simulations.

In this study, by utilizing a model of the polymerization process, the necessary conditions, defined by input of system, initiator concentration and temperature, were determined for producing the polymer within the desired characteristics. The input, that is the reference values of controlled variables, were obtained by means of search algorithm [17]. The mathematical reactor model utilized considers the mains kinetic stages in styrene polymerization [18–21].

The operational conditions obtained by the methodology proposed were implemented by means of a pilot reactor in which an adaptive controller type STC (Self Tuning Controller) was utilized.

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PII S1385-8947(98)00066-7

2. Model of the polymerization reactor

The production of polystyrene in suspension was used to test the proposed method. The kinetic equations that describe the polymerization of styrene by free radicals [18–21] are as follows.

(i) Initiation: peroxide or azocompound

$$I \xrightarrow{K_d} 2R \tag{1}$$

decomposition

$$R+M \xrightarrow{K_i} P_1 \tag{2}$$

(ii) Propagation:

$$P_n+M \xrightarrow{K_p} P_{n+1} \tag{3}$$

(iii) Termination: by combination

$$P_n+P_m \xrightarrow{K_{tc}} D_{n+m} \tag{4}$$

by disproportioning

$$P_n+P_m \xrightarrow{K_{td}} D_n+D_m \tag{5}$$

chain transfer to the monomer

$$P_n+M \xrightarrow{K_f} D_n+P_1. \tag{6}$$

The mass balance for each compound can be written, by neglecting the thermal initiation and by assuming the quasi-stationary hypothesis for the initiator radicals, as:

$$\frac{1}{V}\frac{d([I]V)}{dt} = -K_d[I] \tag{7}$$

$$\frac{1}{V}\frac{d([R]V)}{dt} = -K_i[R][M] + 2fK_d[I] = 0 \tag{8}$$

$$\frac{1}{V}\frac{d([M]V)}{dt} = -K_i[R][M] - K_p[M][P] - K_f[M][P] \tag{9}$$

$$\frac{1}{V}\frac{d([P_1]V)}{dt} = K_i[R][M] - K_p[M][P_1] - K_f[M]([P_1]-[P]) - (K_{tc}+K_{td})[P_1][P] \tag{10}$$

$$\frac{1}{V}\frac{d([P_n]V)}{dt} = K_p[M]([P_{n-1}]-[P_n]) - K_f[M][P_n] - (K_{tc}+K_{td})[P_n][P] \tag{11}$$

$$\frac{1}{V}\frac{d([D_n]V)}{dt} = K_f[M]P_n + K_{td}[P_n][P] + \frac{1}{2}K_{tc}\sum_{m=1}^{n-1}[P_m][P_{n-m}] \tag{12}$$

where $n \geq 2$,

$$[P] = \sum_{n=1}^{\infty}[P_n]$$

and:

$$V = V_0(1+\varepsilon x) \tag{13}$$

$$[M] = \frac{[M_0](1-x)}{1+\varepsilon x} \tag{14}$$

$$\varepsilon = \frac{\rho_m(T)-\rho_p(T)}{\rho_p(T)} \tag{15}$$

and the kinetic parameters are in Appendix A.

The conversion of monomer is calculated solving the system of Eqs. (7)–(12). However, in the current form, this system cannot be solved by direct integration, as n varies within a large range. In order to reduce the system of equations, the moments method [22] was used. By rearranging the equations, the system below is obtained:

$$\frac{d\lambda_0}{dt} = 2fK_d[I] - K_{tc}\lambda_0^2 - \frac{\varepsilon\lambda_0}{1+\varepsilon x}\frac{dx}{dt} \tag{16}$$

$$\frac{d\lambda_1}{dt} = 2fK_d[I] + K_p[M]\lambda_0 + K_f[M](\lambda_0-\lambda_1) - K_{tc}\lambda_0\lambda_1 - \frac{\varepsilon\lambda_1}{1+\varepsilon x}\frac{dx}{dt} \tag{17}$$

$$\frac{d\lambda_2}{dt} = 2fK_d[I] + K_p[M](2\lambda_1+\lambda_0) + K_f[M](\lambda_0-\lambda_2) - K_{tc}\lambda_0\lambda_2 - \frac{\varepsilon\lambda_2}{1+\varepsilon x}\frac{dx}{dt} \tag{18}$$

$$\frac{d\mu_0}{dt} = K_f[M]\lambda_0 + \frac{1}{2}K_{tc}\lambda_0^2 - \frac{\varepsilon\mu_0}{1+\varepsilon x}\frac{dx}{dt} \tag{19}$$

$$\frac{d\mu_1}{dt} = K_f[M]\lambda_1 + K_{tc}\lambda_0\lambda_1 - \frac{\varepsilon\mu_1}{1+\varepsilon x}\frac{dx}{dt} \tag{20}$$

$$\frac{d\mu_2}{dt} = K_f[M]\lambda_2 + K_{tc}(\lambda_0\lambda_2+\lambda_1^2) - \frac{\varepsilon\mu_2}{1+\varepsilon x}\frac{dx}{dt} \tag{21}$$

In the equation system above, the contributions of terminations by disproportioning were not considered, because they are negligible in the case of polystyrene [19,20].

The physical and mechanical properties of the polymer are related to the mean numerical molecular weight (μ_n), mean weighted molecular weight, (μ_w) and polydispersion rate (PD) [22], that are related to the distribution moments of the polymer:

$$\mu_n = \mathrm{PM}\frac{\mu_1}{\mu_0} \quad \mu_w = \mathrm{PM}\frac{\mu_2}{\mu_1} \tag{22}$$

$$\mathrm{PD} = \frac{\mu_w}{\mu_n} \tag{23}$$

where PM is the molecular weight of the monomer unit. In these equations the contribution of the moments of the 'live' polymers was not considered.

Thus, the polymer obtained can be characterized by solving the system of Eqs. (16)–(21) and Eqs. (7) and (9). In order to solve the system of equations, the method of Runge–Kutta–Gill coupled with a step selection algorithm was used.

3. Definition of operational conditions

In the case of a batch polymerization reactor, there are two important factors to be considered in the operational conditions: (i) the final quality of the polymer produced and (ii) the total processing time. The weighting of these two factors in the calculation of input and the complexity of the mathematical model for the polymerization of styrene make it difficult to apply Pontryagin's Maximum Principle in the solution of the problem. For this reason, the search method of Powell [17] was utilized in this study, for the minimization of an objective, defined by the variables that determine the quality of the final polymeric product. Eq. (24) expresses mean weighted molecular weight and the rate of polydispersion, and represents the function that must be minimized to obtain the value of controlled variables:

$$F = [(\mu_w - \mu_{wd})/\mu_{wd}]^2 + [(\mathrm{PD} - \mathrm{PD_d})/\mathrm{PD_d}]^2 \qquad (24)$$

where μ_w is the mean weighted molecular weight, μ_{wd} is the desired mean weighted molecular weight, PD is the polydispersion and $\mathrm{PD_d}$ is the desired polydispersion. The values of these variables at the end of the reaction stage define the quality of the final polymer and, with the conversion, the process time. The resulting problem is one that involves the final value.

In the stage of minimization of Eq. (24), it is necessary to know the values of μ_w and PD at the end of each batch. To do so, it is necessary to have a reliable mathematical model available to predict these variables.

The minimization of Eq. (24) defines the values of concentration of the initiator and of the operation temperature of the reactor that are to produce a polymer with the desired properties [23], observing the restrictions imposed: desired conversion of the monomer and a limit of the processing time.

These restrictions are made in order to prevent the search method from finding solutions with a very long batch time or a very low monomer conversion. In the methodology proposed these restrictions were imposed, by means of a penalty introduced into the search algorithm. This consideration might have been made by introducing these variables into Eq. (24). Nevertheless, to do so, it would be necessary to define the desired values for both the conversion time and the processing time. In the option utilized, a limit is imposed only on those two variables.

Some of the conditions obtained in this experiment are presented in Table 1. It can be observed that for the different conditions desired for the polymer (μ_w and PD) different operational conditions are obtained, in the case of $[\mathrm{I_0}]$ and T. It is also clear that the values obtained for μ_w and PD are very close to the desired ones.

Table 1
The operational conditions

	X (%)	μ_w	PD	T (°C)	I_0 (mol/l)	t (min)	F ($\times 10^6$)
Des	85	280,000	2.00	–	–	–	–
Det	85	280,009	2.02	91.6	0.0105	155	100.0
Des	85	300,000	2.00	–	–	–	–
Det	85	299,818	2.02	87.8	0.0100	201	100.4
Des	87	275,000	2.00	–	–	–	–
Det	87	275,960	2.04	90.8	0.0106	216	412.2
Des	90	180,000	2.20	–	–	–	–
Det	90	179,988	2.20	88.3	0.0044	149	0.004

Des, desired value; Det, determined value.

The model is solved up to some given value of conversion is achieved. When the maximum reaction time is reached or the temperatures go above 100°C, the objective function is penalized by multiplying its value by 10,000. This implies that the values found are not desirable and that a new search must be carried out. The maximum reaction time allowed is 300 min. This is the reaction time usually utilized in industry [19,23,24]. The range of molecular weight and polydispersion of polystyrene, considered desirable in industry, is very wide, depending on the application of the polymer. In the case of polymerization by suspension, which is applied primarily to produce polystyrene for expansion, the reaction is performed in two steps [24]. In the first one, the greater monomer consumption (80 to 90%) occurs and the properties of the polymer are defined. The reaction is preferably completed in the second step, where the expansion agents are added, and the reactor temperature (120–150°C) is greater than in the previous step. This paper is concerned with the first step, which is considered [19,23] to be the critical one. In general, the desired mean weighted molecular weight is between 150,000 and 300,000, and the polydispersion rate is between 1.8 and 2.5. Constraint on the temperature is needed in order to prevent the instability of the suspension. Detailed information can be found in Ref. [24].

4. Experimental unit

The experimental conditions, determined by the minimization Eq. (24), were implemented in a pilot reactor. The experimental unit, shown in Fig. 1, consists of a jacketed reactor of 9.2 l with mechanical agitation and four internal baffles equally spaced. The heat needed is supplied by steam in a plate heat exchanger. The jacket is refrigerated with water.

In Fig. 1, it is shown that the control of the reactor was carried out by using a splint-range control strategy associated with a self-tuning adaptive controller [25]. The control var-

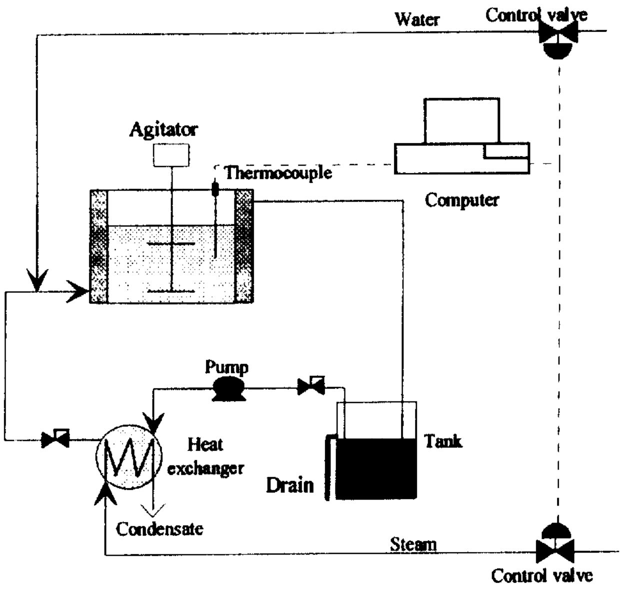

Fig. 1. The pilot-scale unit.

iables, the steam and refrigeration water flow rates, are manipulated through two pneumatic valves.

The system is subject to many kinds of disturbances, such as variations in steam pressure, variations in environment temperature, increase in viscosity of the reacting medium, due to the gel effect, incrustations on the reactor wall, etc.

5. STC controller

The second stage of automation and control involves the design and implementation of a control strategy, capable of maintaining the desired operational conditions. Due to the peculiarities of batch polymerization reactors, mainly their non-linear behavior, the existence of a gel effect and absence of a well-defined stationary operation state, it is necessary to utilize an adaptive controller. In this experiment, the STC of Clarke and Gawthorp [25] was used.

For the STC that was utilized, adaptive control is based on two stages of calculation: first, the recursive estimation of the parameters of the model assumed for the process, and second, the calculation of the control action that optimizes the performance rate. The self-tuning adaptive controller (STC) determines the control action through minimization of the following criterion of performance.

$$I=E\{[P(q^{-1})Y(t+\mathrm{Tm})-R(q^{-1})W(t)]^2 + [Q(q^{-1})U(t)]^2\} \qquad (25)$$

where E is the mathematical expectation, $W(t)$ is the reference value, $U(t)$ is the manipulated variable, Tm is the dead time, and $P(q^{-1})$, $R(q^{-1})$ and $Q(q^{-1})$ are the design parameters of the controller, which are polynomials that define the quality of the control action to be implemented and $Y(t+\mathrm{Tm})$ is the value of the controlled variable, predicted for the instant t + Tm through the recursive model of the process type ARMA (Auto-Regressive and Moving Average) represented by Eq. (26):

$$A(q^{-1})Y(t)=B(q^{-1})+U(t-\mathrm{Tm})+C(q^{-1})\xi(t) \qquad (26)$$

where $A(q^{-1})$, $B(q^{-1})$ and $C(q^{-1})$ are polynomials. $Y(t)$ is a controlled variable. $U(t-\mathrm{Tm})$ is a manipulated variable and $\xi(t)$ are noises present in the process.

The law of control is deduced using the optimum predictor $Y^*(t+\mathrm{Tm}|_t)$, which predicts the output of the process some Tm moments ahead. The optimum predictor for Eq. (26) is deduced in Appendix B and can be expressed by Eq. (27):

$$Y^*(\mathrm{t}+\mathrm{Tm}|_t) = \frac{F'(q^{-1})Y(t)+E(q^{-1})B(q^{-1})U(t)+\gamma}{C(q^{-1})} \qquad (27)$$

where γ is a compensation factor in $E(q^{-1})$ and $F'(q^{-1})$ are defined in Appendix B. By definition, the prediction error can be calculated by Eq. (28):

$$e(t+\mathrm{Tm})=Y(t+\mathrm{Tm})-Y^*(\mathrm{t}+\mathrm{Tm}|_t) \qquad (28)$$

It can be demonstrated that $e(t+\mathrm{Tm})$ is not correlated with $Y(t)$, $Y(t-1)$. Therefore, Eq. (25) can be written in the form of Eq. (29). For $P(q^{-1})\mathrm{e}(t+\mathrm{Tm})$ is not correlated with $Y^*(t+\mathrm{Tm}|_t)$.

$$I=\{[P(q^{-1})Y(t+\mathrm{Tm}|_t)-R(q^{-1})W(t)]^2 + [Q(q^{-1})U(t)]^2+E[P(q^{-1})e(t+\mathrm{Tm})]^2\} \qquad (29)$$

Thus the problem is reduced to a deterministic optimization. Consequently, the minimum of I comes to be determined equaling its gradient to zero, in this way obtaining Eq. (30):

$$b_0[P(q^{-1})Y^*(\mathrm{t}+\mathrm{Tm}|_t)-R(q^{-1})W(t)] + q_0Q(q^{-1})U(t)=0 \qquad (30)$$

When the parameters of the system are known, the law of control can be determined, substituting Eq. (27) with Eq. (30).

Defining $Q_1(q^{-1})$ by means of the equation below:

$$Q_1(q^{-1})=b_0^{-1}q_0Q(q^{-1}) \qquad (31)$$

the vector ψ^* $(t+\mathrm{Tm})$ can be defined by:

$$\psi^*(\mathrm{t}+\mathrm{Tm}|_t)=P(q^{-1})Y^*(\mathrm{t}+\mathrm{Tm}|_t) - R(q^{-1})W(t)+Q_1(q^{-1})U(t) \qquad (32)$$

With this, it is established that the law of optimum control can be determined as follows:

$$\psi^*(\mathrm{t}+\mathrm{Tm}|_t)=0 \qquad (33)$$

Clarke and Gawthrop [25] showed that an optimization problem equivalent to that formulated with Eq. (29) is solved by extending the concept of an optimum predictor to ψ^* and how the same law of control is applied by minimizing the following criterion of performance:

$$J=E\{\psi^2(t+\mathrm{Tm}|_t)\}=\psi^{*2}(\mathrm{t}+\mathrm{Tm}|_t)+E\{[P(q^{-1})e(t+\mathrm{Tm})]^2\} \quad (34)$$

Therefore, substituting Eq. (B.5) into Eq. (32) and premultiplying by $C(q^{-1})$, we get:

$$C(q^{-1})\psi^*(\mathrm{t}+\mathrm{Tm}|_t)=F(q^{-1})Y(t)+G(q^{-1})U(t)+H(q^{-1})W(t)+\gamma \quad (35)$$

Since ψ^* $(t+\mathrm{Tm})$ is to be reduced to zero at every sampling interval, we have:

$$F(q^{-1})Y(t)+G(q^{-1})U(t)+H(q^{-1})W(t)+\gamma=0 \quad (36)$$

The control action $U(t)$ can be calculated from Eq. (36), as long as $F(q^{-1})$, $G(q^{-1})$, $H(q^{-1})$ and γ are known. However, discrete models for chemical processes are not usually known, thus making it necessary to identify them and estimate their parameters, from which the law of control can be calculated recursively. In this investigation, the method of minimum recursive squares was utilized to estimate these parameters, which is the most utilized algorithm for making estimates in adaptive control.

6. The tuning of STC

Although STC is an adaptive controller, its performance depends on its design parameters, that is, the polynomials $P(q^{-1})$, $Q(q^{-1})$, $R(q^{-1})$ of Eq. (25) must be defined.

For the STC, the definition of these parameters is of utmost importance and characterizes the quality of control obtained. In this study, a procedure was utilized, which, from Kc, Ti and TD projected by a digital PID, it is possible to define the coefficients of $P(q^{-1})$, $Q(q^{-1})$, $R(q^{-1})$, parameters of the STC design [23,26]. In this way, the control law of a PID is imposed on the STC. Thus it is possible to utilize for this STC the design and adjustment techniques existing for the PID.

The proposal is based on a comparison between the control law of the PID and the equation of the STC design.

From the control law of a digital PID written in the form of velocity [27] and defining, as the initial adjustment of the STC, the polynomials $P(q^{-1})$, $Q(q^{-1})$, $R(q^{-1})$, we obtain:

$$P(q^{-1})\equiv \mathrm{Kc}\left\{\left[1+\frac{\mathrm{Ts}}{\mathrm{Ti}}+\frac{\mathrm{Td}}{\mathrm{Ts}}\right]-\left[1+2\frac{\mathrm{Td}}{\mathrm{Ts}}\right]q^{-1}+\frac{\mathrm{Td}}{Ts}q^{-2}\right\} \quad (37)$$

$$R(q^{-1})\equiv \mathrm{Kc}\left(\frac{\mathrm{Ts}}{\mathrm{Ti}}\right) \quad (38)$$

$$Q(q^{-1})\equiv 1-q^{-1} \quad (39)$$

Thus, the design polynomials of the STC are completely defined by the PID parameters [23,26].

Although this adjustment may impose some limitations on STC, considering that with other polynomials different from those obtained by this method of adjustment, controllers with superior performance can be obtained, nothing more than an initial adjustment is intended, so that a more complex controller can later evolve, in case it should be needed.

In order to determine the parameters of the PID used in this work, an identification of the system in open loop was performed. With the resulting model, the ITAE methodology [27] was applied in order to obtain the initial parameters.

7. Experimental results

The operation of a polymerization reactor is subjected to several problems. However, the main problem in batch polymerization reactors is the gel effect [18,19]. This effect is directly related to kinetic reactions and changes significantly the viscosity of the reaction medium. This can lead to instabilities during the operation. In order to compensate for possible changes in the processing conditions, an adaptive self-tuning controller was used [25,26].

The recursive least-squares method was used for the estimation of parameters, with a forgetting factor of 0.97. The system was identified in an open loop by introducing a step-type disturbance in the position of both of the valves. In this experiment, the reactor was filled with water, and the transfer function was approximated by a first-order expression with dead time. The identification of the system is performed with the reactor filled with water in order to obtain the approximation of a model. If this identification were performed with the reactor filled with the reaction medium, the reaction could be set in motion, with the consequent loss of suspension.

For validation of the control strategy, the experimental conditions determined for a batch with 87% conversion, as shown in Table 1, were implemented in the pilot unit. Table 2 shows the operational conditions of the pilot-scale unit.

Table 3 shows the parameters of the self-tuning controller used in the temperature control of the reactor. These parameters were obtained by adjusting the self-tuning controller to rules used for a proportional integral derivative (PID) controller.

After filling the reactor with water and the suspension agent, the system was heated to the temperature of 85°C. At

Table 2
The reactor operational conditions

Parameter	Value
Temperature (°C)	90.8
Demineralized water (l)	4.2
Styrene (l)	1.8
Initiator (benzoyl peroxide) (mol/l)	0.0106
Tri-calcium phosphate (g)	10.45
Agitation (rpm)	2000
Reaction time (min)	216

Commercial styrene (EDN SA), 99.75%.
Benzoyl peroxide and tri-calcium phosphate quality P.A.

Table 3
The STC parameters

Parameter	Value
n	1
m	1
λ	0.97
Tm	4
Sample time (s)	10
$P(q^{-1})$	$(210/200-q^{-1})$
$Q(q^{-1})$	$1-q^{-1}$
$R(q^{-1})$	$10/200$

this point, styrene was added. The initiator was only added when the set-point temperature (90.8°C) was reached.

Fig. 2 shows the performance of the temperature controller operating at the conditions presented in Table 1. It can be observed that the controller was able to follow the whole cycle of the batch reaction, mainly the transition stage between the initial heating and the beginning of the reaction, without showing overshoot. The controller was also able to maintain the temperature constant during the operation, by compensating the heat produced by the reaction and the alterations in the global heat exchange coefficient due to the increase in the viscosity of the reaction medium and incrustation on the reactor wall.

Fig. 3 shows the control action of opening the steam and water valves during the reaction. It can be seen that the position of the valves does not achieve any steady state during the operation cycle. This is one of the main difficulties in the design and implementation of control systems for batch reactors.

A sample was withdrawn when the reaction time achieved 216 min (12,960 s) and a gel permeation chromatographic analysis was performed in a Waters 600E Chromatography. Table 4 compares the characteristics of the final polymer with the desired characteristics considered in the objective function. The deviations are within the acceptable range for experimental data. Thus, it is possible with the proposed method to previously define the qualities of the polymer. Further tests were performed in order to find out other characteristics from Table 1. The results presented deviations similar to those depicted in Table 4, which proves the reliability of the proposed methodology.

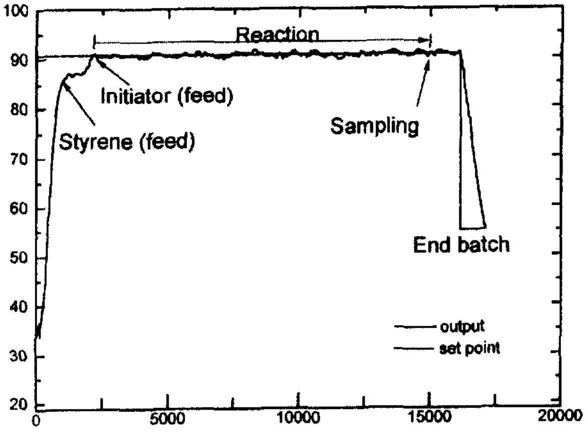

Fig. 2. Performance of the controller.

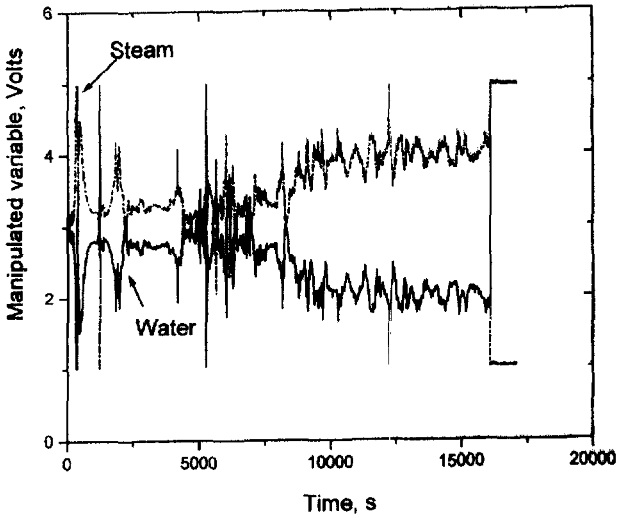

Fig. 3. Control action (1 V, 100% closed valve; 5 V, 100% open valve).

Table 4
Comparison between the desired and experimental properties

Parameter	Des	Det	Exp	Err (%)
PD	2.00	2.04	1.91	6.75
μ_w	275,000	275,960	289,577	4.70
x	87%	87%	89.8%	3.11
t (min)	216	216	216	–

Des, Desired value.
Det, Determined value.
Exp, Experimental value.
Err, Experimental × optimized.

8. Final remarks

A general methodology was applied that allows a previous definition of the operational conditions in order to obtain a product with certain desired properties. This methodology is a very important tool for the operation of polymerization reactors and meets the quality demands for the final product.

The proposed technique can be enhanced by the sophistication of the mathematical model of the reactor. This can be done by the introduction of thermofluid-dynamic aspects within the modeling, as well as by the use of different search algorithms, without, however, overloading the computational effort.

As regards the performance of the STC controller (adjusted to the parameters of the classic PID), its satisfactory operation was observed in all the steps of the process: the warm-up step, the reaction step and, finally, the cooling step. The STC was capable of adapting to the changes in the dynamics of the process and its performance was quite strong, considering the large number of disturbances introduced.

Acknowledgements

R.A.F. Machado acknowledges the financial support given by CAPES.

Appendix A. Kinetic parameters

$\rho_m = 919.3 - 0.665(T - 273.15)\,(g/l)$

$\rho_p = 992.6 - 0.265(T - 273.15)\,(g/l)$

$K_d = 1.027 \times 10^{16} \exp(-30/RT)\,(\mathrm{min}^{-1})$

$K_f = 1.422 \times 10^{6} \exp(-7.816/RT)\,(\mathrm{mol/lmin})$

$K_{to} = 2.646 \times 10^{11} \exp(-2.268/RT)\,(\mathrm{mol/lmin})$

$K_t = g_t K_{to}$

$$g_t = \begin{cases} 1 & 0 \le x < 30, \\ \exp[-2(A_1 x + A_2 x^2 + A_3 x^3)], & 30 \le x \le 80 \end{cases}$$

$A_1 = 2.57 - 5.05 \times 10^{-3} T$

$A_2 = 9.56 - 1.76 \times 10^{-2} T$

$A_3 = -3.03 + 7.85 \times 10^{-3} T$

$f_0 = 0.5$

$$f = \frac{f_0^2 \left(\frac{[M]}{[M_0]} \right)^2}{2(1 - f_0) \frac{[I]}{[I_0]}} \left[\left(1 + \frac{4(1 - f_0) \frac{[I]}{[I_0]}}{f_0^2 \left(\frac{[M]}{[M_0]} \right)^2} \right)^{1/2} - 1 \right]$$

$\mathrm{Kp} = 1.422 \times 10^{9} \exp(-7.06/RT)$ (mol/l min)
PM = 104.14 (g/mol)

Appendix B. Optimum predictor

The optimum predictor is obtained several steps ahead, considering the model given by Eq. (26), multiplying by $E(q^{-1})$:

$$E(q^{-1})A(q^{-1})Y(t+\mathrm{Tm}) = E(q^{-1})B(q^{-1})U(t) + E(q^{-1})C(q^{-1})\xi(t+\mathrm{Tm}) + E(q^{-1})\gamma \quad (B.1)$$

where $E(q^{-1})$ satisfies the Diophantina equation, below:

$$C(q^{-1}) = E(q^{-1})A(q^{-1}) + q^{-\mathrm{Tm}}F'(q^{-1}) \quad (B.2)$$

with $E(q^{-1}) e F'(q^{-1})$ given by:

$$E(q^{-1}) = 1 + e_1 q^{-1} + \ldots + e_{\mathrm{Tm}-1} q^{1-\mathrm{Tm}} \quad (B.3)$$

$$F'(q^{-1}) = f_0' + f_1' q^{-1} + \ldots + f_{n-1}' q^{1-n} \quad (B.4)$$

By substituting Eq. (B.2) into Eq. (B.1) *e* considering that the components $\xi(t+\mathrm{Tm})$ are in the future, the optimum predictor is obtained, as shown below:

$$C(q^{-1})Y^*(t+\mathrm{Tm}|_t) = F'(q^{-1})Y(t) + E(q^{-1})B(q^{-1})U(t) + E(q^{-1})\gamma \quad (B.5)$$

Using the definition of ψ^* given in Eq. (32) and substituting it in Eq. (B.5), we have:

$$\begin{aligned} C(q^{-1})\psi^*(t+\mathrm{Tm}|_t) &= P(q^{-1})F'(q^{-1})Y(t) \\ &+ [P(q^{-1})E(q^{-1})B(q^{-1}) \\ &+ C(q^{-1})Q_1(q^{-1})]U(t) \\ &- C(q^{-1})R(q^{-1})W(t) + P(q^{-1})E(q^{-1})\gamma \end{aligned} \quad (B.6)$$

from which the projection equation below arises:

$$C(q^{-1})\psi^*(t+\mathrm{Tm}|_t) = F(q^{-1})Y(t) + G(q^{-1})U(t) + H(q^{-1})W(t) + \gamma' \quad (B.7)$$

where:

$$F(q^{-1}) = P(q^{-1})F'(q^{-1}) \quad (B.8)$$

$$G(q^{-1}) = P(q^{-1})E(q^{-1})B(q^{-1}) + C(q^{-1})Q_1(q^{-1}) \quad (B.9)$$

$$H(q^{-1}) = -C(q^{-1})R(q^{-1}) \quad (B.10)$$

$$\gamma'(q^{-1}) = P(q^{-1})E(q^{-1})\gamma \quad (B.11)$$

Appendix C. Nomenclature

$A(q^{-1})$	Polynomial in q^{-1}
$B(q^{-1})$	Polynomial in q^{-1}
$C(q^{-1})$	Polynomial in q^{-1}
$[D_i]$	Concentration of 'dead' polymeric chains
E	Mathematical expectation
f	Efficiency factor of the initiator
I	STC performance criteria
$[I_0]$	Initial concentration of initiator, mol/litter
$[I]$	Concentration of initiator, mol/litter
$[M_0]$	Initial concentration of monomer, mol/litter
$[M]$	Concentration of monomer, mol/litter
PD	Polidyspersion
$[P_i]$	Concentration of 'live' polymeric chains
PM	Molecular weight of monomer, g/mol
$P(q^{-1})$	Parameter of STC project
$Q(q^{-1})$	Parameter of STC project
R	Concentration of initiator radicals, mol/litter
$R(q^{-1})$	Parameter of STC project
T	Temperature, °C or K
Tm	Dead time
U	Manipulated variable
V_0	Volume of organic phase, at $x = 0$, litter
V	Volume of organic phase, litter
x	Conversion
$Y(t)$	Controlled variable
$Y(t+\mathrm{Tm})$	Variable predicted for the instant $t + \mathrm{Tm}$

Greek letters

ε	Contraction factor
γ	Compensation factor
λ_k	k-th moment of 'live' polymer
μ_k	k-th moment of 'dead' polymer
μ_n	Mean numerical molecular weight
μ_w	Mean weighted molecular weight
$\rho_m(T)$	Density of monomer (g/l)
$\rho_p(T)$	Density of polymer (g/l)
ξ	Noises present in the process

References

[1] M.E. Sacks, S. Lee, II, J.H. Biesenberger, Chem. Eng. Sci. 28 (1973) 241–257.
[2] G.Z.A. Wu, L.A. Denton, R.L. Laurence, Polym. Eng. Sci. 22 (1982) 1–8.
[3] B.M. Louie, D.S. Soong, J. Appl. Polym. Sci. 30 (1985) 3707–3749.
[4] B.M. Louie, D.S. Soong, J. Appl. Polym. Sci. 30 (1985) 3825–3840.
[5] T. Takamatsu, S. Shioya, Y. Okada, Ind. Eng. Chem. Res. 27 (1988) 93–99.
[6] S.-S. Jang, W.-L. Yang, Chem. Eng. Sci. 42 (1989) 2429–2436.
[7] Y.J. Huang, L.J. Lee, Chem. Eng. Sci. 44 (1989) 363–376.
[8] A. Penlidis, J.F. MacGregor, A.E. Hamielec, Chem. Eng. Sci. 44 (1989) 273–281.
[9] V.K. Tzouanas, S.L. Shah, Chem. Eng. Sci. 44 (1989) 1183–1193.
[10] L.S. Henderson, R.A. Cornejo, Ind. Eng. Chem. Res. 28 (1989) 1644–1653.
[11] J.-S. Chang, J.-L. Lai, Ind. Eng. Chem. Res. 31 (1992) 861–868.
[12] D.J. Kozub, J.F. MacGregor, Chem. Eng. Sci. 47 (1992) 929–942.
[13] D.J. Kozub, J.F. MacGregor, Chem. Eng. Sci. 47 (1992) 1047–1062.
[14] G. Maschio, T. Bello, C. Scali, Chem. Eng. Sci. 47 (1992) 2609–2614.
[15] S. Carafilakis, MSc Thesis/COPPE/Federal University of Rio de Janeiro, Brazil (in Portuguese) 1993.
[16] A.Y.-D. Tsen, S.S. Jang, D.S.H. Wong, B. Joseph, AIChE J. 42 (1996) 455–465.
[17] J.L. Kuester, J.H. Mize, MacGraw-Hill, NY, 1973.
[18] J.A. Biesenberger, D.H. Sebastian, Wiley, NY, 1983.
[19] G. Odian, Wiley, NY, 1991.
[20] G. Kalfas, W.H. Ray, Ind. Eng. Chem. Res. 32 (1988) 1822–1830.
[21] Z.L. Wang, F. Pla, J.P. Corriou, Chem. Eng. Sci. 50 (1995) 2081–2091.
[22] W.H. Ray, J. Macrom. Chem. C8 (1) (1972) 1–52.
[23] R.A.F. Machado, MSc Thesis/ENQ/Federal University of Santa Catarina, Brazil (in Portuguese) 1996.
[24] R.B. Bishop, Cahners Publishing, MA, 1971.
[25] D.W. Clarke, P.J. Gawthrop, Proc. IEEE 122 (1975) 929–934.
[26] A. Bolzan, DSc Thesis, COPPE/Federal University of Rio de Janeiro, Brazil (in Portuguese) 1991.
[27] E.D. Seborg, T.F. Edgar, D.A. Mellichamp, Series in Chemical Engineering, Wiley, NY, 1989.