On-Line Optimization of Free Radical Bulk Polymerization Reactors in the Presence of Equipment Failure

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ABSTRACT: An on-line optimizing control scheme has been developed for bulk polymerization of free radical systems. The effects of random errors, as well as one kind of a major disturbance (heating system failure), have been studied. A model-based, inferential state estimation scheme was incorporated to estimate, on-line, the parameters of the model (and thereby, the monomer conversion and molecular weight of the polymer) using experimental data on temperature and viscosity. A sequential quadratic programming technique was used for this purpose. A major disturbance, such as heating system failure, leads to a deteriorated final product unless an on-line optimal temperature trajectory (history) is recomputed and implemented on the reactor. Genetic algorithm was used for this purpose. It has been found that, if the "sensing" of the major temperature deviation from the optimal value and rectification of the heating system is achieved well in advance of the onset of the Trommsdroff effect, use of a reoptimized temperature history is sufficient to produce the desired product without significantly altering reaction time. However, if such a disturbance occurs late, a single-shot intermediate addition of an optimal amount of initiator needs to be used in addition to changing the temperature history to produce polymers having the desired properties in the minimum reaction time. Other types of failures can similarly be handled using the methodology developed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2101-2120, 1999

Key words: optimization; on-line optimization; bulk polymerization; inferential state estimation; genetic algorithm

INTRODUCTION

Most industrial polymerization reactors operate under nonisothermal and/or semibatch conditions and their operating conditions are based on some optimality criteria. Generally, these conditions are based on intuition or experience; but, with the vast knowledge-base now available, appropriate models can easily be developed and optimizing control can be implemented on current reactors to improve their performance. In this study, we explore the feasibility of an optimizing control scheme for a sample polymerization system, poly-(methyl methacrylate) (PMMA). The procedures developed herein can easily be used for other free radical polymerization reactors.

The availability of a transport phenomenabased analytical model is a prerequisite to developing a scheme for optimizing control. Over the last several years, a considerable amount of research has been reported in the open literature on models for polymerization of methyl methacrylate (MMA). This system follows the standard kinetic scheme (Table I) with termination primarily by disproportionation (i.e., $k_{tc} \approx 0$). The gel (or

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Initiation	$I \xrightarrow{k_d} 2R$
	$R + M \xrightarrow{k_i} P_1$
Propagation	$P_n + M \xrightarrow{k_p} P_{n+1}$
Termination by	$P_n + P_m \xrightarrow{k_{tc}} D_{n+m}$
combination	
Termination by disproportionation	$P_n + P_m \rightarrow D_n + D_m$
Chain transfer to monomer	$P_n + M \xrightarrow{k_f} P_1 + D_n$
Chain transfer to monomer	$P_n + S \xrightarrow{k_s} S + D_n$
via solvent	$S + M \xrightarrow{\text{fast}} S + P_1$
	or
	$P_n + M \xrightarrow{k_s} D_n + P_1$

Table I	Kinetic	Scheme	for	Addition
Polymer	ization			

 $k_{tc},\,k_{f},\,{\rm and}\,k_{s}$ are taken as zero in the present study (bulk polymerization of MMA).

Trommsdorff^{1,2}), glass, and cage effects are also exhibited in the bulk polymerization of MMA. The gel effect arises because of the decrease in k_{td} at high monomer conversions, x_m , associated with increased diffusional resistance to the growing radicals. It is manifested as a sudden increase in x_m (as well as the weight average molecular weight, M_w) with time, t, after some polymerization has occurred. Similarly, the glass effect is associated with the decrease of k_p due to increased diffusional resistance to the movement of the monomer toward a growing radical. This leads to the polymerization stopping short of complete monomer conversion, even though the reactions are irreversible. The cage effect is associated with increasing resistance to the diffusion of the primary radicals away from each other due to the increasing viscosity of the medium at high conversions. The resulting waste reactions (not incorporated in the kinetic scheme) lead to a decrease in the initiator efficiency, f.

Chiu and colleagues³ developed a molecular model using the Fujita–Doolittle free-volume theory to explain the diffusional limitations of the termination and propagation rate constants. Achilias and Kiparissides^{4,5} adapted this model using the free-volume theory of Vrentas and Duda,⁶ and modeled the diffusional effects on k_t and k_p , as well as the initiator efficiency. Neither of these models are applicable to industrial reactors that operate under nonisothermal or semibatch conditions. This is because the rate constants and/or the initiator efficiency are correlated to the *initial values* of the number average chain length, $\mu_{n,0}$, or the initial concentration of the initiator, $[I]_0$, which are not precisely defined for such conditions. Ray and colleagues⁷ and Seth and Gupta⁸ developed improved models that did not have these limitations. Using experimental data^{9,10} under isothermal conditions and taken in small glass ampoules, they obtained curve-fit correlations for two⁷ or three⁸ model parameters, $\theta_t(T), \theta_p(T), \text{ and } \theta_t(T)$. The model predictions are found to be in good agreement with experimental data taken in a 1-L Parr® reactor under nonisothermal¹¹ and semibatch¹² conditions. No retuning of the best-fit correlations developed using data from small glass ampoules is required. This suggests that the model accounts for all the physicochemical phenomena associated with polymerization quite well.

The model of Seth and Gupta⁸ can be used for optimization and control studies. Indeed, some studies along these lines have been reported recently. Chakravarthy and colleagues¹³ used a newly emerging and an extremely robust technique, called genetic algorithm (GA), ^{14–16} to compute optimal temperature histories that minimize the reaction time, t_f , whereas simultaneously satisfying the requirements (endpoint constraints) that the final monomer conversion, x_{mf} , and the final value of the number average chain length, μ_{nf} , approach the desired values, x_{md} and μ_{nd} , respectively. The optimization technique is quite fast, and the solutions are reasonably close to the global optimum. Hence, this technique can be used for on-line optimizing control of large-scale polymerization reactors, provided we can estimate the state of the system on-line. Densitometers and gel permeation chromatography have been used on-line in some experimental control studies¹⁷⁻¹⁹ of solution polymerizations for estimating $x_m(t)$ and $\mu_n(t)$ or $\mu_w(t)$. For bulk polymerizations, however, these experimental techniques cannot be used conveniently; hence, model-based inferential state estimation techniques (called software sensors) have to be used. Embirucu and colleagues²⁰ reviewed the open literature on advanced control strategies for polymerization reactors and found that very few studies had been reported on property estimation techniques for *bulk* polymerizations. Kiparissides and Morris²¹ also emphasized the need for reliable predictive models for on-line state estimation. Seth and Gupta⁸ and Chakravarthy and colleagues¹³ suggested the use of experimental val-

ues of the viscosity, $\eta(t)$, along with the temperature, T(t), for on-line estimation of monomer conversion and number average chain length. Bhargava Ram and colleagues²² demonstrated feasibility of such a scheme. They used a movinghorizon inferential state estimation technique to study bulk polymerization of MMA with "pseudo"experimental data on $\eta(t)$ and T(t) (generated from a model, with noise superimposed). The correlation of Lyons and Tobolsky,²³ as suggested by Moritz,²⁴ was used for this purpose. The sequential quadratic programming (SQP) method was used to obtain best-fit values of the parameters $(\theta_t, \theta_p, \theta_f)$ of the model, using $\eta(t)$ and T(t) in a short estimation horizon and the state variables, $x_m(t)$, $\mu_n(t)$, and $\mu_w(t)$, were predicted for future times. They²² established, using simulations, that the (reverse) prediction of the state of the system, in terms of x_m and M_w , from viscosity and temperature data $[\eta_{exp}(t)]$ and $T_{exp}(t)$ is unique, provided the prediction is model-based. It is to be noted that the $\eta_{\exp}(t)$ values reflect not only the effect of temperature, but also M_w and the concentration of the polymer in the reaction mass.

In this article we extend the work of Bhargava Ram and colleagues²² and study, theoretically, the feasibility of implementing on-line optimizing control for a bulk MMA polymerization reactor. An optimal temperature history is first computed (off-line), using GA. This is implemented along with "equipment failure" on the reactor model and "experimental" values of $\eta(t)$ and T(t) are obtained and stored. Details of generation of experimental data are discussed later. These data are then used in the forward direction starting from t = 0 to implement on-line optimizing control. Periodic checks are made using an error criterion based on deviation of the temperature from desired values to "sense" (and rectify) major failures or disturbances (e.g., failure of the heating system, etc.). Whenever such disturbances are sensed, model parameters are estimated and a new optimal temperature history (to be implemented *thereafter*) is computed. This is then implemented. The procedure is repeated until polymerization is complete. The methodology developed herein is very general and can be used for a variety of conditions (e.g., for positive and negative temperature failures, etc.). Only a few examples are presented in this work. It is to be emphasized that we have used pseudoexperimental values (model values with noise as well as effects of major disturbances added) of $\eta(t)$ and T(t) to demonstrate the feasibility of such a scheme for

Table IICage, Gel, and Glass Effect Equationsfor Bulk Polymerizations4,5,8

$$\frac{1}{f} = \frac{1}{f_0} \left[1 + \theta_f(T) \frac{M}{V_1} \frac{1}{\exp[\xi_{I3}\{-\psi + \psi_{\text{ref}}\}]} \right]$$
(1)

$$\frac{1}{k_{td}} = \frac{1}{k_{td,0}} + \theta_t(T)\mu_n^2 \frac{\lambda_0}{V_1} \frac{1}{\exp[-\psi + \psi_{\text{ref}}]}$$
(2)

$$\frac{1}{k_p} = \frac{1}{k_{p,0}} + \theta_p(T) \frac{\lambda_0}{V_1} \frac{1}{\exp[\xi_{13}\{-\psi + \psi_{\text{ref}}\}]}$$
(3)

$$\mu = \frac{\gamma \left\{ \frac{\rho_m \phi_m V_m^*}{\xi_{13}} + \rho_p \phi_p \hat{V}_p^* \right\}}{\rho \phi_p \hat{V}^* V_p + \rho \phi_p \hat{V}^* V_p}$$
(4)

$$\psi_{\rm ref} = \frac{\gamma}{V_{\rm c.}} \tag{5}$$

$$V_1 = \frac{M(MW_m)}{\rho_m} + \frac{(\xi_{m1} - M)(MW_m)}{\rho_n}$$
(6)

$$\phi_m = \frac{M(MW_m)/\rho_m}{\frac{M(MW_m)}{\rho_m} + \frac{(\xi_{m1} - M)(MW_m)}{\rho_p}}$$
(7)

$$\phi_p = 1 - \phi_m \tag{8}$$

$$\hat{V}^*(MW)$$

$$\xi_{13} = \frac{v_m (M \, W_m)}{\hat{V}_p^* M_{jp}} \tag{9}$$

$$\xi_{I3} = \frac{V_I^*(MW_I)}{\hat{V}_*^*M_{in}} \tag{10}$$

$$k_d = k_d^0 \exp(-E_d/RT) \tag{11}$$

$$k_{p,0} = k_{p,0}^0 \exp(-E_p/RT)$$
(12)

$$k_{td,0} = k_{td,0}^0 \exp(-E_{td}/RT)$$
(13)

Viscosity Equations

$$\begin{split} \eta &= \eta_{\rm sol} \Bigg[1 + C_{\rm polym}[\eta] \exp \biggl(\frac{k_H [\eta] C_{\rm polym}}{1 - b C_{\rm polym}} \biggr) \\ &+ C_{\rm polym}^2 [\eta]^2 \exp \biggl(\frac{2k_H [\eta] C_{\rm polym}}{1 - b C_{\rm polym}} \biggr) \Bigg] \quad (14) \\ C_{\rm polym} &= \rho_p \phi_p \end{split}$$

$$[\eta] = KM_w^a \tag{16}$$

on-line optimizing control (henceforth, we will use the term, *experimental* values instead of *pseudoexperimental* values). Work on the *actual* implementation of this code on a lab-scale reactor is in progress.

FORMULATION

The scheme for on-line optimizing control involves four basic steps: (1) integration of model equations, (2) generation of optimal temperature

Table III Parameters Used for Bulk Polymerization of MMA with AIBN²²

$$\begin{split} \rho_m &= 966.5 - 1.1 \; (T \; - \; 273.15) \; \mathrm{kg \; m^{-3}} \\ \rho_p &= 120 \; \mathrm{kg \; m^{-3}} \\ f_0 &= 0.58 \\ k_d^0 &= 1.053 \times 10^{15} \; \mathrm{s^{-1}} \\ k_d^{0,0} &= 4.917 \times 10^2 \; \mathrm{m^3 \; mol^{-1} \; s^{-1}} \\ k_{td,0}^0 &= 9.8 \times 10^4 \; \mathrm{m^3 \; mol^{-1} \; s^{-1}} \\ k_{tc} &= 0.0 \\ k_f &= 0.0 \\ k_i &= k_p \\ k_s &= 0.0 \\ E_d &= 128.45 \; \mathrm{kJ \; mol^{-1}} \\ E_p &= 18.22 \; \mathrm{kJ \; mol^{-1}} \\ E_{td} &= 2.937 \; \mathrm{kJ \; mol^{-1}} \\ (MW_m) &= 0.10013 \; \mathrm{kg \; mol^{-1}} \\ (MW_I) &= 0.06800 \; \mathrm{kg \; mol^{-1}} \end{split}$$

Parameters for Cage, Gel, and Glass Effects

$$\begin{split} \rho_m \hat{V}_I^* &= 9.13 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1} \\ \hat{V}_M^* &= 8.22 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1} \\ \hat{V}_p^* &= 7.70 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1} \\ M_{jp} &= 0.18781 \text{ kg mol}^{-1} \\ \gamma &= 1 \\ V_{fm} &= 0.149 + 2.9 \times 10^{-4} \left[T(K) - 273.15 \right] \\ V_{fn} &= 0.0194 + 1.3 \times 10^{-4} \left[T(K) - 273.15 - 105 \right]; \text{ for } T < 105 + 173.15) K \end{split}$$

Mark-Houwink Constants for Intrinsic Viscosity

$$K = 6.75 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$$

 $a = 0.72$

K and a assumed to be (almost) independent of T

Parameters for the Modified Lyons-Tobolsky Equation

$$\begin{split} k_{H} &= -d_{1} + d_{2}T \\ d_{1} &= 0.3118 \\ d_{2} &= 9.93 \times 10^{-4} \text{ K}^{-1} \\ b &= -3.5 \times 10^{-3} \text{ m}^{3} \text{ kg}^{-1} \text{ (assumed independent of } T) \\ \eta_{\text{sol}} &= \exp(-0.099 + 496/T)/T^{1.5939} \text{ Pa} \cdot \text{s} \end{split}$$

Correlations Used for Curve-Fitting and Parameters Used at t = 0

 $\begin{array}{rl} \log_{10}[\theta_t(T),\,\mathrm{s}] = a_1 - a_2(1/T) &+ a_3(1/T^2) \\ \log_{10}[\theta_p(T),\,\mathrm{s}] = b_1 - b_2(1/T) &+ b_3(1/T^2) \\ \log_{10}[10^3\theta_\mathrm{f}(T),\,\mathrm{m}^3\,\mathrm{mol}^{-1}] = c_1 - c_2(1/T) &+ c_3(1/T^2) \\ \end{array}$ $\begin{array}{rl} a_1 &= 1.2408 \,\times \,10^2; & a_2 \,= \, 1.0314 \,\times \,10^5; & a_3 \,= \, 2.2735 \,\times \,10^7 \\ b_1 &= \, 8.0593 \,\times \,10^1; & b_2 \,= \, 7.5000 \,\times \,10^4; & b_3 \,= \, 1.7650 \,\times \,10^7 \\ c_1 &= \, 2.0160 \,\times \,10^2; & c_2 \,= \, 1.4550 \,\times \,10^5; & c_3 \,= \, 2.7000 \,\times \,10^7 \end{array}$



Figure 1 A typical temperature history showing the terminology used.

histories, (3) generation of experimental data on temperature and viscosity, and (4) state estimation. These are first described. Thereafter, the logic used for control is presented.

Model

The general kinetic scheme for free radical polymerizations is given in Table I. The mass balance and moment equations for polymerization in a semibatch reactor are given in ref. 13 and are not repeated herein. These are in the form of ordinary differential equations and can be written in the following general form

$$d\boldsymbol{x}/dt = \boldsymbol{F}(\boldsymbol{x}, \, \boldsymbol{u}) \tag{1a}$$

$$\boldsymbol{x}(t = t_{\text{init}}) = \boldsymbol{x}_{\text{init}}$$
(1b)

where $\boldsymbol{x}(t)$ is the state variable vector defined, for bulk polymerizations, by

$$\boldsymbol{x} = [I, M, R, \lambda_0, \lambda_1, \lambda_2, \mu_0, \mu_1, \mu_2, \zeta_{m1}]^T \quad (2)$$

and u(t) is the control variable vector [in the present case, it is a scalar, T(t)]:

$$\boldsymbol{u}(t) = \boldsymbol{u}(t) = \boldsymbol{T}(t) \tag{3}$$

 λ_k and μ_k (k = 0, 1, 2, ...) represent the *k*th moments of the chain-length distributions of the radical and dead macromolecular species, P_n and D_n , respectively (see Nomenclature for definitions). ζ_{m1} is an additional variable that gives the total moles of liquid monomer added starting from t = 0 until time, *t*. \boldsymbol{x}_{init} is the value of \boldsymbol{x} at an initial value of time, $t_{init} \cdot t_{init}$ could either be 0 or an intermediate value. The conversion of monomer is defined as

$$x_m = 1 - (M/\zeta_{m1})$$
(4)

Table II gives the expressions^{4,5,8} for the initiator efficiency, f, and for the rate constants, k_p



Figure 2 Temperature history (T_{ref}) for the reference case. Also shown are the "experimental" data, T_{exp} , for $0 \le t \le t_B$, as well as for $t \ge t_B$ (temperature increased empirically to T_{ref}). The reoptimized temperature points, T_{rop} , are also shown.

and k_{td} . They are observed to have the following general form:

$$k_{td} = k_{td}(\boldsymbol{x}, \, \boldsymbol{u}, \, \boldsymbol{\rho}) \tag{5a}$$

$$k_p = k_p(\boldsymbol{x}, \, \boldsymbol{u}, \, \boldsymbol{\rho}) \tag{5b}$$

$$f = f(\boldsymbol{x}, \, \boldsymbol{u}, \, \boldsymbol{\rho}) \tag{5c}$$

with

$$\boldsymbol{\rho} = [\theta_t, \ \theta_p, \ \theta_f]^T \tag{6}$$

The values of several parameters required to integrate the model equations are given in Table III for bulk polymerization of MMA using 2'2-azobis(isobutyronitrile) (AIBN) initiator. The three parameters $[\theta_t(T), \theta_p(T), \text{ and } \theta_f(T)]$ are expressed in terms of second-order polynomials in 1/T (see Table III).

Model equations can be integrated for any specified temperature history (linear interpolation of temperature is used where it is available in digitized form), using the NAG library program D02EJF based on Gear's technique.²⁵ Integration leads to x_m , μ_n , and μ_w histories for $t_{\text{init}} \leq t \leq t_f$. The modified Lyons–Tobolsky²³ equation [eq. (14), Table II] can then be used to predict the viscosity, η , of the reaction mass. This equation relates η to the temperature, T, and to the other state variables characterizing the system (x_m and M_w).

Optimization

The optimal temperature history, $T_{opt}(t)$; $t_{init} \leq t \leq t_f$, is obtained by solving the following general optimization problem:



Figure 3 Variation of viscosity with time for one temperature history shown in Figure 2. Notation the same as in Figure 2.

$$\text{Min } I[T(t)] = [(t_f - t_{\text{init}}) + w_1 (1 - x_{mf}/x_{md})^2 \\ + w_2 (1 - \mu_{nf}/\mu_{nd})^2]$$
(7a)

subject to:

 $d\mathbf{x}/dt = \mathbf{F}(\mathbf{x}, u);$ $\mathbf{x}(t = t_{\text{init}}) = \mathbf{x}_{\text{init}}$ (7b)

$$u_{\min} \le u(t) \le u_{\max} \tag{7c}$$

In the above equation, I is the objective function to be minimized, and w_1 and w_2 are weightage factors that are assigned large values to force the endpoint values, x_{mf} and μ_{nf} , of the monomer conversion and the number average chain length, to approach their desired values, x_{md} and μ_{nd} , closely. The endpoint requirement on x_m forces the amount of unreacted monomer to be small, and hence keeps postreactor separation and recycling costs low. The constraint on μ_{nf} leads to the production of polymer having desired properties, because several physical properties of polymers are related to their values of μ_n . A review of optimization studies on addition polymerizations is provided by Louie and Soong.²⁶ The objective function given in eq. (7a) has been used by several workers (e.g., Chakravarthy and colleagues,¹³ Sachs and colleagues,²⁷ Farber and Laurence,²⁸ and Vaid and Gupta²⁹). GA has been used¹³ for solving eq. (7) for the MMA system (for $t_{\text{init}} = 0$). Details of the algorithm are available in ref. 13. Minimization of I gives the optimal temperature history required to minimize the *remaining* reaction time, $t_f - t_{\text{init}}$, while satisfying the endpoint and other (system) constraints.

Generation of Experimental Data

We now describe the technique to generate experimental data on T(t) and $\eta(t)$ for a single major disturbance (heating system failure) considered in this work. Both random errors, as well as (major) disturbances, need to be incorporated in the smooth optimal temperature history, $T_{opt}(t)$, and in the cor-



Table IV Flow Chart Used for On-Line Optimizing Control

responding $\eta(t)$ history, to reflect the operation of real reactors. Before this is done, however, we need to describe the zones into which the time, t, is to be divided. Figure 1 shows two such zones. t_B is the value of t at which the effect of a (single) major disturbance is *sensed* (sensing is assumed to imply rectification of the failure also, in this work). The optimal temperature history is recomputed for the period thereafter. t_B , thus, represents the end of the first zone. A major disturbance is assumed to have occurred at t_A , and it takes some additional time, $(t_B - t_A)$, for its effect to be sensed. The criterion of sensing the major disturbance in this figure is a deviation of 5°C from the optimal value. $t_B - t_A$ is



Figure 4 Number average chain length versus time for the case shown in Figure 3.

the time taken (270 s in this case) for temperature of the reactor to drop below the specified deviation.

The (smooth) optimal temperature history, $T_{opt}(t)$, for $0 \le t \le t_f$ is obtained using the *current* values of the coefficients,²² a_1 , b_1 , c_1 , and d_1 (referred to as a_1-d_1) given in Table III. This is shown in Figure 1 by the solid curve. While implementing the optimal temperature history, the effect of major disturbance on the temperature history is then superimposed (for $t > t_A$) on the temperature. The temperature for $t > t_A$ is modeled empirically using a cubic equation

$$T(t) = p_1 + p_2 t + p_3 t^2 + p_4 t^3; \qquad t \ge t_A \quad (8)$$

The values of the coefficients, p_i , are chosen such that continuity of temperature is maintained at t_A . Also, the coefficients in eq. (8) are chosen such that the fall in temperature represents real-life situations. It is also assumed that the temperature falls thereafter, by $\sim 5^{\circ}$ C in ~ 5 min. The exact equation used (for $t_A \leq t \leq t_A + 300$) is

$$T(t) = 83.4301 - 0.259245 t - 0.190874$$
$$t^{2} + 0.0120371 t^{3} \quad (9)$$

Random (experimental) error is now added on to the (smooth) temperature history adapted for the (major) disturbances as described herein. A sampling time, Δt , of 0.5 min is selected. The value of the *experimental* temperature at any time, t_i^* , is obtained using

$$T_{\exp}(t_j^*) = T(t_j^*) + [R_{j,1}(t_j^*) - 0.5]$$
(10)

where $T(t_j^*)$ is given by eq. (9) and $R_{j,1}$ is a random number between 0 and 1, generated using the NAG subroutine, G05CCF. The term $R_{j,1}(t_j^*)$ - 0.5 is used to obtain noise having an amplitude of ± 0.5 °C. Figure 2 shows $T_{\exp}(t_j^*)$ for $0 \le t$ $\le t_B$.

The model equations are integrated from t = 0 s using the experimental values, $T_{\exp}(t_j^*)$ (with linear interpolation between adjacent experimental points), and the current values of a_1 -



Figure 5 Monomer conversion versus time for the case shown in Figure 3.

 d_1 , to give model-predicted values of $\eta(t)$. There is a certain degree of smoothening achieved during integration. It is necessary, therefore, to introduce random errors into the values of $\eta(t)$ using

$$\eta_{\rm exp}(t_i^*) = \eta(t_i^*) [0.1R_{i,2}(t_i^*) + 0.95]$$
(11)

where $R_{j,2}$ is a random number between 0 and 1. Use of eq. (11) leads to fluctuations in values of η_{\exp} of $\pm 5\%$. Figure 3 shows randomized viscosity data for $0 \leq t \leq t_B$. It may be added that data on $T_{\exp}(t_j^*)$ and $\eta_{\exp}(t_j^*)$ need to be generated for a sufficient period of time beyond the introduction of the disturbance. At every value of t_j^* , the following error check is made:

$$|T_{\exp}(t_{j}^{*}) - T_{\mathrm{opt}}(t_{j}^{*})| < \in$$
 (12)

where \in is a preassigned deviation from the reference trajectory. The moment this criterion is violated, it is assumed that the disturbance has

been sensed. This defines the value of t_B . Experimental points of T and η beyond this time can be discarded.

Inferential State Estimation

State estimation is conducted using the entire set of experimental points, $T_{\exp}(t_j^*)$ and $\eta_{\exp}(t_j^*)$ in the estimation horizon, $0 \le t \le t_B$. Best-fit values of the four parameters, a_1-d_1 , are thus obtained. These need not be the same as the reference values²² given in Table III, because retuning of these parameters is expected to take care of any deficiencies of the model. SQP is used for the parameter estimation. The objective function, E, to be minimized for the curve-fitting of viscosity data is taken as

(13a)

$$\begin{array}{l} \text{Min } E(a_1, \ b_1, \ c_1, \ d_1) \\ = \sum_{i = (t_{\text{nif}}/\Delta t) + 1}^{i = (t_{\text{B}}/\Delta t) + 1} \left[\frac{\eta_{\exp}(i) - \eta_{\text{th}}(i)}{\eta_{\text{th}}(i)} \right]^2 \end{array}$$



Figure 6 Weight average chain length versus time for the case shown in Figure 3.

subject to:

 $d\mathbf{x}/dt = \mathbf{F}(\mathbf{x}, u);$ $\mathbf{x}(t = t_{\text{init}}) = \mathbf{x}_{\text{init}}$ (13b)

$$a_{1,L} \le a_1 \le a_{1,U} \tag{13c}$$

$$b_{1,L} \le b_1 \le b_{1,U}$$
 (13d)

$$c_{1,L} \le c_1 \le c_{1,U}$$
 (13e)

$$d_{1,L} \le d_1 \le d_{1,U} \tag{13f}$$

Equation (13b) is integrated with $T_{\exp}(t)$ for current values of a_1-d_1 and the Lyons–Tobolsky equation is used to provide the theoretical values, $\eta_{\rm th}(t)$, of the viscosity. The detailed procedure has been described by Bhargava Ram and colleagues.²² The state of the system (x_m, μ_n, μ_w) can, thus, be inferred from the model using the best-fit values of a_1-d_1 so estimated.

Scheme for On-Line Optimizing Control

We have presented details on the four major steps required for on-line optimizing control, namely, integration of the model equations, generation of optimal temperature histories, generation of experimental temperature and viscosity data, and inferential state estimation. We now describe the detailed procedure for accomplishing the control. Table IV gives the basic flow chart describing the logic used.

An (off-line) optimized temperature history, $T_{opt}(t)$ or $T_{ref}(t)$, based on literature values²² of a_1-c_1 is assumed to be implemented on the reactor, starting from t = 0 s (see Fig. 1). Experimental temperature and viscosity data are continuously recorded (generated in this study). These data incorporate scatter as well as effects of major disturbances. The moment the experimental value of the temperature, $T_{exp}(t)$, is found to deviate by a prescribed value (\in) from the desired optimal value [as per eq. (12)], it is assumed that the major disturbance has been sensed. The entire experimental data [$T_{exp}(t)$ and $\eta_{exp}(t)$] in this



Figure 7 Reoptimized temperature histories for $\in = 3^{\circ}$ C and 5°C. Also shown are the reference history and experimental data points ($0 \le t \le t_{B1}$ or t_{B2}).

zone is then used to obtain best-fit values of the parameters, a_1-d_1 , of the model (model-based inferential state estimation). These parameters are used to compute a reoptimized temperature history, $T_{\rm rop}(t)$, for the next zone, which is implemented. Figure 1 shows $T_{\rm rop}(t)$ after introducing random errors, for $t_B \leq t \leq t_f$. The procedure is continued until the polymerization is complete. Additional major disturbances can be incorporated in a manner analogous to the procedure described herein.

State estimation and the calculation of the optimal temperature history, thus, is based on experimental temperature and viscosity values. These will not be affected by reactor fouling, provided the mixing of the reactor contents is effective (e.g., using anchor or ribbon agitators) so as to avoid spatial variations in the reactor. The presence of impurities, however, would require the inclusion of additional reactions in the kinetic scheme shown in Table I. A few additional parameters associated with these reactions will need to be incorporated in the model and subsequently estimated on-line. The same methodology can then be used for optimizing control even for these cases.

RESULTS AND DISCUSSION

The computer code developed for on-line optimizing control of free radical polymerization reactors (PMMA in the present study) was run for the following endpoint constraints:

$$x_{md} = 0.94$$

 $\mu_{nd} = 1850$
subject to:
 $60^{\circ}C \leq T(t) \leq 90^{\circ}C$ (14)



Figure 8 Monomer conversion histories corresponding to the temperature histories shown in Figure 7.

These values are quite close to those used by Chakravarthy and colleagues,¹³ and Vaid and Gupta,²⁹ as well as other workers. The optimal temperature history, $T_{opt}(t) = T_{ref}(t)$, was generated for $0 \le t \le t_f$ using GA and is shown by the solid curve in Figure 2. The final reaction time for this smooth optimal temperature history was 1656.56 s ($\equiv t_{f,ref}$), whereas the final values, μ_{nf} and x_{mf} , were 1854.99 and 0.9354 (= $\mu_{nf,ref}$; $x_{mf,ref}$, respectively, quite close to the desired values given in eq. (14). A major disturbance (heating system failure) at $t = t_A = 360$ s and lasting for 270 s (until $t = t_B = 630$ s), was then superimposed on $T_{ref}(t)$. Heating was restarted after 630 s. The rate of heating was chosen em*pirically*, such that the temperature returns to $T_{\rm ref}(t)$ (see Fig. 2). The reactor temperature was kept at $T_{ref}(t)$ thereafter. Random errors of amplitude ± 0.5 °C were then superimposed on the entire temperature history to simulate actual experimental data in the presence of the failure of the heating system. Figure 2 shows these experimental "data" points as $T_{exp}(t_{j}^{*})$. The values of the number average chain length and the monomer conversion at time $t = t_{f,ref} = 1656.56$ s for the experimental temperature history were found to be 1177.47 and 0.5420, respectively. Both these values are observed to be quite far from the values of $\mu_{nf,ref}$ and $x_{mf,ref}$. This indicates that the effect of a major disturbance is quite significant. We find, however, that the value of $\mu_{nf,ref}$ is indeed obtained at a larger value of time, t= 1687.20 s, but the value of x_{mf} at this point is only 0.8813. Similarly, it is found that the final value of the monomer conversion for $T_{exp}(t)$ is equal to 0.9354 ($= x_{mf,ref}$) at t = 1768.80 s, but at this point, μ_{nf} is found to be 1965.44, which is far in excess of $\mu_{nf,ref}$. Thus, it is evident that the desired final characteristics of the product cannot be attained by simply returning to $T_{ref}(t)$ after the major failure, and one must use a reoptimized temperature history. This was achieved using the computer code for on-line optimizing control developed in this work. The value of \in [eq. (12)] was



Figure 9 Reoptimized temperature history for $t_A = 900$ s, for two values of \in (cases **A** and **B**). Reference temperature history also shown.

taken as 5°C (in fact, the value of t_B of 630 s was obtained using this value of \in). It is assumed that the heating system resumed normal functioning right after $t = t_B$, the point at which the major disturbance is sensed, implying that a very short real-time is required for computing the reoptimized temperature history.

Before actually obtaining the reoptimized temperature history, $T_{rop}(t)$, for $t_B \leq t \leq t_f$, "experimental" data on viscosity for $0 \leq t \leq t_B$ are generated [using $T_{exp}(t)$ for this period only], as previ-

Table VComparison of Results for \in = 5°Cand \in = 3°C for $t_{\rm A}$ = 900 s

Variable	\in = 5°C	\in = 3°C
$\begin{array}{c}t_B\\t_f\\\mu_n\\x_{mf}\end{array}$	1200.00 s 1737.37 s 1913.83 0.9032	1110.00 s 1693.83 s 1897.60 0.9115

ously described. Data points for $T_{exp}(t)$ and $\eta_{exp}(t)$ for $0 \le t \le t_B$ (Figs. 2 and 3) are used to curve-fit (inferential state estimation) the values of the model parameters, a_1 - d_1 . These parameters are used to obtain $T_{rop}(t)$ for the period $t_B \leq t \leq t_{f}$. Figure 2 shows this reoptimized temperature history (with random noise superimposed). The final reaction time, t_{f} for the reoptimized case was found to be 1685.25 s, slightly larger than the reference value of 1656.56 s. The final values of the number average chain length and the monomer conversion were found to be 1859.19 and 0.9320, respectively, which compare quite well with the reference case. This was the best one could achieve. It is to be noted that, in the absence of reoptimization, the endpoint constraints on both μ_n and x_m could not be satisfied simultaneously. This indicates the superiority and the necessity of reoptimizing the temperature history on-line after a major failure is sensed. Figure 3 also shows the (randomized) experimental values of $\eta_{\exp}(t)$ for $t_B \leq t \leq t_f$ using $T_{rop}(t)$. Figures 4–6



Figure 10 Reoptimized temperature history for the case associated with prolonged failure ($t_B = 2160$ s). Experimental data points for $0 \le t \le t_B$ shown along with the reference temperature history.

show the corresponding plots for $\mu_n(t)$, $x_m(t)$, and $\mu_w(t)$ for the temperature histories:

$$T(t) = T_{exp}(t); \qquad 0 \le t \le t_B$$
$$= T_{rop}(t); \qquad t_B \le t \le t_f \qquad (15)$$

To study the sensitivity of the system to \in , the failure of the heating system was assumed to occur at t = 360 s. The value of \in was taken as 3°C. It was found that use of an *empirical* temperature history [similar to $T_{\exp}(t_j^*)$ in Fig. 2] with $\in = 3$ °C, leads to the satisfaction of the endpoint constraints, although this is achieved at higher values of t_f of 1800 s, than for the reference run. However, use of a reoptimized temperature history (see Fig. 7) leads to even better results. It is found that the final reaction time, t_f , for the reoptimized temperature history is 1658.38 s, which is almost equal to that for the reference case. The

final values of the number average chain length and the monomer conversion were found to be 1855.25 and 0.9355, respectively. These terminal values are also quite close to the reference case and so are satisfactory. The advantage of on-line optimizing control is again observed. Figure 8 compares $x_m(t)$ for the on-line optimized temperature histories for the two values of \in . A comparison of $T_{rop}(t_j^*)$ for $\in = 3^{\circ}$ C and 5° C (Fig. 7) shows that the optimal temperature for $\in = 5^{\circ}$ C starts from a lower level (near $t_{B,2}$), but then rises to higher values than for $\in = 3^{\circ}$ C.

Figure 9 shows $T_{rop}(t)$ when t_A , the point of failure of the heating system, is changed from 360 s to 900 s, a point somewhat close to the onset of the gel effect than in the case shown in Fig. 2. Two values of \in , 5°C and 3°C, are studied. The reoptimized temperature histories are shown for two values of \in studied, 5°C and 3°C, which were sensed at $t_{B,A}$ and $t_{B,B}$, respectively. The values

Case	$I_{\rm add}~({\rm mol}~{\rm m}^{-3})^{\rm a}$	$t_{f}\left(\mathbf{s} ight)$	μ_{nf}	x_{mf}	Remarks
А	0.0	1737.37	1913.83	0.9032	No IA
$t_{\rm A} = 900 \ {\rm s}$	$2.8660 imes10^3$	1680.80	1887.60	0.9180	
$t_{\rm B} = 1200 \ {\rm s}$	$3.8660 imes10^3$	1680.80	1880.93	0.9240	
$\tilde{\in} = 5^{\circ}C$	$5.8660 imes10^3$	1680.80	1863.40	0.9338	
	$6.8660 imes10^3$	1709.09	1854.11	0.9381	Best solution
	$9.8660 imes10^3$	1878.78	1853.81	0.9374	
В	0.0	1693.84	1897.60	0.9115	No IA
$t_{\rm A} = 900 \ {\rm s}$	$6.8660 imes10^3$	1810.61	1859.31	0.9340	
$t_{\rm B} = 1110 \ {\rm s}$	$7.8660 imes10^3$	1839.79	1852.30	0.9370	Best solution
$\in = 3^{\circ}C$					
С	0.0	2680.40	2086.77	0.7884	No IA
$t_{\rm A} = 360 \ {\rm s}$	$2.8527 imes10^3$	2475.95	2068.47	0.7868	
$t_{\rm B} = 2160 \ {\rm s}$	$6.8527 imes10^3$	2475.95	2055.41	0.7914	
$T_{\rm B}-T_{\rm A}=3^{\circ}{\rm C}$	$9.8527 imes10^3$	2475.95	2055.41	0.7914	

Table VI Effect of IA of Initiator-Monomer Solution $([I]_0 = 15.48 \text{ mol m}^{-3})$

 ${}^{a}I_{add}$ represents the mol of initiator added to 1 m³ of the original reaction mixture at $t = t_{B}$ (in the form of a 10-ml initiator-monomer solution).



Figure 11 Reoptimized temperature histories for two cases (cases A and B) involving optimal intermediate addition of initiator. Reference temperature history also shown.



Figure 12 Number average chain length versus time corresponding to the three cases shown in Figure 11.

of t_f , μ_{nf} , and x_{mf} for these cases are given in Table V. These results in Table V suggest that the endpoint constraints cannot be satisfied in these cases and that an additional control variable, for example, intermediate addition of initiator, may be necessary to satisfy the endpoint constraints. Figure 10 shows $T_{rop}(t)$ when the cooling of the reactor is slower than that assumed in Fig. 2, and a much larger value of $t_B - t_A$ of 1800 s is used. This also leads to a late implementation of reoptimization. It may be noted that we are not invoking eq. (12) in this case, because t_B occurs far beyond the reference value of t_{f} . Thus, this case represents a prolonged failure of the heating system, for a fixed period of time. The final values for this run (case C) are found to be

$$t_f = 2680.40 \text{ s}$$

 $\mu_{nf} = 2086.77$
 $x_{mf} = 0.7884$ (16)

Again, it is found that the endpoint constraints cannot be met by temperature changes alone, and that, *possibly*, intermediate addition of initiator is required as an additional control variable. The relatively lower temperatures $[T_{rop}(t)$ in Figs. 9 and 10] near the end of the reaction is associated with a preponing of the Trommsdorff effect leading, in turn, to a lower value of t_f (the endpoint constraints are not being satisfied anyway).

We also conducted on-line optimizing control of the MMA polymerization reactor using two control variables—T(t) and a *one-time* intermediate addition of a 10^{-2} m³ solution of initiator in monomer, added for every 1 m³ of the reaction mixture. This intermediate addition (IA) of the initiatormonomer solution is done at $t = t_B$, the point at which the major failure is sensed. Continuity conditions for the mass and energy balance equations can easily be written for the IA case (see ref. 8). Table VI summarizes the results obtained for cases **A**, **B**, and **C** previously described [corresponding to Table V and eq. (16)]. It is observed



Figure 13 Monomer conversion versus time for the three cases shown in Figure 11.

that an optimal value of initiator addition (I_{add}) = 6.8660×10^3 mol m⁻³) is indicated from our study for case A. In this case, the endpoint constraints are met satisfactorily, while minimizing t_f to 1709.09 s. This value is only slightly higher than the value of 1656.56 s for the reference run where major disturbances are not present. Table VI also shows that an optimal $I_{
m add}$ of 7.8660 imes 10 3 mol m⁻³ is necessary for the case when $\in = 3^{\circ}C$ (case **B**). Figures 11–13 show $T_{rop}(t)$, $\mu_n(t)$, and $x_m(t)$ for the case where an optimal amount of initiator is added during polymerization for these two cases. These have been compared with $T_{ref}(t)$. The intermediate addition of initiator results in a postponement of the Trommsdroff effect, compared with the reference case. It is interesting to observe the complex interaction of the two control mechanisms being used (temperature and initiator addition) in obtaining optimal solutions.

Table VI, case C shows that, for a *very* late sensing of the effect of heating system failure shown in Figure 10, a one-time IA does not suffice. Multiple addition of the initiator-monomer solution at later stages would possibly not serve much purpose, because improper mixing, due to high viscosity, would impair product quality. We believe that it would not be possible to save these batches from going "off-spec." Cases involving other failures that require "negative initiator additions" can be similarly handled using *pure* monomer addition. This will effectively reduce the initiator concentration.

A methodology for on-line state-estimation and optimization of free radical polymerizations has been presented in this work. Its use has been illustrated for a sample case of failure leading to a fall in the reactor temperature, T(t). The technique is general and can be used as effectively for other types of failures. It is expected that the effect of such failures, when sensed, will have to be negated by using temperature histories different from the off-line computed histories. In addition to the above, it may also be necessary to adjust the initiator concentration in certain cases.

CONCLUSIONS

The present work establishes the feasibility of implementing on-line optimizing control of free radical polymerization reactors (PMMA semibatch reactors in the present work) to produce polymers of desired properties in the shortest reaction time. A few examples of major disturbances and random errors were incorporated to reflect the operation of real reactors. After the major disturbances were sensed, the model parameters were updated and used to infer, online, the state of the system (model-based inferential state estimation). The optimal temperature history for future times was again obtained using updated values of the model parameters and then implemented on the reactor model. It has been shown that if the major failure (involving a lowering of the temperature) is sensed early enough, compared with the onset of the Trommsdroff effect, intermediate initiator addition with an optimal temperature history could lead to the production of the desired polymer in an optimal manner. Other failures can be handled in a similar manner.

NOMENCLATURE

a	parameter in Mark–Houwink equa-
	tion
$a_1 - a_3$	parameters in correlation of θ_t
$a_{1,L} - a_{1,U}$	lower and upper bounds on a_1
$b_1 - b_3$	parameters in correlation of θ_p
$b_{1,L} - b_{1,U}$	lower and upper bounds on b_1
$C_{\rm polvm}$	concentration of polymer (kg m^{-3})
$c_1 - c_3$	parameters in correlation of θ_f
$c_{1,L} - c_{1,U}$	lower and upper bounds on c_1
D_n	dead polymer molecule having n
	repeat units
$d_1 - d_2$	parameters in correlation of k_H
$d_{1,L} - d_{1,U}$	lower and upper bounds on d_1
E	objective function
E_d, E_p, E_t	activation energies for initiation,
*	propagation, and termination in
	the absence of gel or glass effects
	$(kJ mol^{-1})$
f	initiator efficiency at time t
f_0	initiator efficiency in the limiting
	case of zero diffusional resis-
	tance
Ι	objective function, moles of initia-
	tor at any time $t \pmod{t}$

$I_{\rm add}$	initiator	added	(intermediate)
	(mol m	-3)	
K	parameter	· in Mark	-Houwink equa-

- parameter in Mark–Houwink equation (m³ kg⁻¹)
- k_H Huggin's constant, dimensionless k_d, k_p, k_t rate constants for initiation, propagation, and termination in the presence of the gel and the glass effects (s⁻¹ or mol⁻¹ s⁻¹)
- $k_d^0, k_{p,0}^0, k_{t,0}^0$ frequency factors for initiation, propagation, and termination in the absence of gel and glass effects (s⁻¹ or m³ mol⁻¹ s⁻¹)
- $k_{t,0}, k_{p,0}$ k_t and k_p in the absence of gel or glass effects (m³ mol⁻¹ s⁻¹)
- M moles of monomer in the liquid phase (mol)
- M_{jp} molecular weight of polymer jumping unit (kg mol⁻¹)
- M_n number average molecular weight $[\equiv (MW_m)(\lambda_1 + \mu_1)/(\lambda_0 + \mu_0),$ kg mol⁻¹]
 - weight average molecular weight $[\equiv (MW_m)(\lambda_2 + \mu_2)/(\lambda_1 + \mu_1),$ kg mol⁻¹]
- M_{WI}, M_{WM} molecular weights of pure initiator and monomer (kg mol⁻¹) P_n growing polymer radical having n
 - repeat units primary radical, universal gas
 - constant (atm m³ mol⁻¹ K⁻¹) temperature of the reaction mixture (K)
 - time (s)

 M_{m}

R

t

 t_A

 t_B

 t_C

 t_f

 Δt

u

T(t)

- time at which major disturbance is introduced (s) time at which major disturbance is
- sensed (s) time after which empirical trajec-
- tory follows optimal history (s)
 - final reaction time (s)
- sampling time (s) control vector (scalar, u, in this
 - work) volume of liquid at time t (m³)
- V_1 volume of liquid at time $t (m^3)$ V_{fm}, V_{fp} fractional free volumes of monomer and polymer in the reaction mixture
- $\hat{V}_{I}^{*}, \hat{V}_{m}^{*}, \hat{V}_{p}^{*}$ specific critical hole free volume of initiator, monomer, and polymer $(m^{3} \text{ kg}^{-1})$

 w_1, w_2 weightage factors

$$oldsymbol{x}$$
 vector representing state variables $x_m(t)$ monomer conversion (molar) at time t

Greek

\in	allowed temperature deviation (K)		
γ	overlap factor		
η	viscosity of reaction mass $(Pa \cdot s)$		
$[\eta]$	intrinsic viscosity $(m^3 kg^{-1})$		
$\eta_{ m sol}$	solvent (monomer) viscosity (Pa \cdot s)		
$\zeta_{\rm m1}$	net monomer added to the reactor		
$\theta_t, \ \theta_p, \ \theta_f$	adjustable parameters in the model (s,		
. ,	s, and $m^3 mol^{-1}$)		
λ_k	kth ($k = 0, 1, 2,$) moment of live		
	(P_n) polymer radicals		
	$\equiv \sum n^k P_n$, (mol)		
	n = 1		
μ_k	kth ($k = 0, 1, 2,$) moment of		
	dead (D_n) polymer chains		
	[∞]		
	$\equiv \sum n^k D_n, (\text{mol})$		
	$\begin{bmatrix} n=1 \end{bmatrix}$		
μ_n	number average chain length at time $t = (1 + 1)^{1/2} (1 + 1)^{1/2}$		
	$u_1 = (\chi_1 + \mu_1)/(\chi_0 + \mu_0)$		
μ_w	weight average chain length at time $t = (\lambda + \mu)/(\lambda + \mu)$		
εε	$\iota_1 = (\kappa_2 + \mu_2)/(\kappa_1 + \mu_1)$		
5 13, 5 13	mor and initiator jumping units to		
	the critical molar volume of the		
	nolymer respectively		
0	vector representing the model param-		
Ρ	eters θ_{1} θ_{2}		
0 0	density of pure (liquid) monomer and		
Pm, Pp	polymer at temperature T (kg m ⁻³)		
φ	volume fractions of monomer and poly-		
rmr + p	mer in liquid at time t		
ψ. ψ _{maf}	free volume parameters		
,, Trei	r		

Subscripts/Superscripts

ddesired values exp experimental values final values (at $t = t_f$) f init initial value maximum value max min minimum value opt optimum value ref reference value reoptimized value rop $^{\mathrm{th}}$ theoretical value

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