

On-Line Optimizing Control of Bulk Polymerization of Methyl Methacrylate: Some Experimental Results for Heater Failure

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ABSTRACT: An experimental unit has been assembled to carry out on-line optimizing control of the bulk polymerization of methyl methacrylate (MMA). A rheometer–reactor assembly is used. Temperature and viscosity measurements are used to describe the state of the system. The polymerization is carried out under an off-line computed optimal temperature history, $T_{\text{op}}(t)$. A planned disturbance (heating system failure) is introduced at time t_1 . This disturbance leads to a fall in the temperature of the reaction mass. A new optimal temperature history, $T_{\text{reop}}(t)$, is re-computed *on-line* and is implemented on the reaction mass at time t_2 , when the heating is resumed. This procedure helps ‘save the batch’. A genetic algorithm is used to compute this reoptimized temperature history in a short period of ~ 2 min of *real* time. The feasibility of the on-line optimizing control scheme has been demonstrated experimentally. Replicable results for the viscosity history, $\eta(t)$, of the polymerizing mass under several non-isothermal conditions have been obtained. These experimental results are quite trustworthy, even though the model predictions are only in approximate agreement with them, perhaps because of the extreme sensitivity of results to the values of the model parameters. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2350–2360, 2002

Key words: optimization; genetic algorithm; PMMA; polymerization; on-line optimal control

INTRODUCTION

The physical properties of any commodity plastic depend largely on its molecular weight distribution (MWD). Generally, from the point of view of product application, it is desirable to have high weight-average molecular weight, M_w , products with a narrow MWD. Martin et al.¹ and Nunes et al.² have shown that narrowing the MWD improves the thermal properties, stress–strain relationships, impact resistance, and hardness and

strength of the polymer. To produce such materials in industrial reactors, we need to measure the ‘state’ of the reaction mass (e.g., polymer concentration, M_w , etc.) continuously as the polymerization proceeds and take corrective action whenever there are any ‘disturbances’ to planned operation. Unfortunately, experimental measurements of the polymer concentration and the MWD (or the average molecular weights) *on-line* are not easy, particularly for bulk polymerizations,^{3,4} and easy-to-measure secondary variables need to be used to provide reliable inferential measurements of these quantities. In our earlier work,^{5–7} we reported how the viscosity, η , of the reaction mass (or any related property, like the electrical power required for stirring the reaction mass) and the temperature, T , at time, t , both of which are easily

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measured, could be used along with a mathematical model for the polymerization and with appropriate correlations for η , as software sensors to infer the state of the system. In fact, we developed a rheometer–reactor assembly and reported experimental values of η versus t during polymerization of a free radical system under a variety of temperature histories and using different values of the initiator loading, I_o . A sample system, namely, methyl methacrylate (MMA)-azobis isobutyronitrile (AIBN) was used. Correlations were developed for η as a function of T , monomer conversion, x_m , and M_w (the latter two being obtained using a kinetic model). The Martin equation⁷ was modified to the following form and used:

$$\eta = \eta_{\text{sol}}[1 + \eta_{\text{int}}c_{\text{polym}}\exp\{d_0 + d_1(\eta_{\text{int}}c_{\text{polym}}) + d_2(\eta_{\text{int}}c_{\text{polym}})^2\}] \quad (1)$$

In this equation, η_{sol} is the viscosity of pure solvent (monomer in this case) in Pa s, η_{int} is the intrinsic viscosity (at a reference temperature, and so related to M_w through the Mark–Houwink equation), c_{polym} is the polymer concentration (related to x_m), and d_0 , d_1 , and d_2 are parameters (depending on T and I_o) that are determined⁷ by curve-fitting experimental data on $\eta(t)$ with a least-squares fit. The correlations for these parameters (d_0 , d_1 , and d_2), developed using experimental data under three different (isothermal) temperatures, predicted $\eta(t)$ under non-isothermal (off-line computed) optimal temperature histories extremely well,⁷ without any re-tuning of the parameters. Thus, it was inferred that $\eta(t)$ and $T(t)$ data could, indeed, be used as an appropriate software sensor. In fact, Bhargava Ram et al.⁸ have shown that the state of the system (x_m and M_w) can be predicted *uniquely* using $\eta(t)$ and $T(t)$, as just described, and can be used for on-line optimizing control of polymerizations.

The feasibility of model-based on-line inferential state estimation and optimal control has been demonstrated⁹ *theoretically* for batch reactors producing poly(methyl methacrylate), PMMA, using corrective action [implementing a reoptimized temperature history, $T_{\text{reop}}(t)$, after sensing a heating-system failure] to ‘save the batch’ (give product with the originally planned values of x_m and M_w even after the disturbance, in as short a remaining period as possible). Theoretically generated (“*pseudo-experimental*”) data were used for this purpose. What still needs to be demonstrated is the efficacy of such control for *experi-*

mental polymerizations. This study is a step in this direction.

In this work, we compute (off-line) an optimal temperature history, $T_{\text{op}}(t)$, using a genetic algorithm (GA)^{10–13} to produce PMMA with desired properties (final values of the number-average chain length, final $\mu_n = \mu_{\text{nd}}$, and monomer conversion, final $x_m = x_{\text{md}}$), in the minimum reaction time, t_f . This computed temperature history is implemented experimentally. During polymerization, the experimental temperature history, $T(t)$, and the viscosity history, $\eta(t)$, are recorded continuously. We then introduce a planned disturbance (heater failure) in the system, sense it, compute a reoptimized temperature history, $T_{\text{reop}}(t)$ on-line (using GA), and implement this on the reactor as soon as the electrical power becomes available. The experimental data on $T(t)$ and $\eta(t)$ are used to find out if the scheme works experimentally. The reason we used GA is it is an extremely robust technique and gives solutions that are quite close to the global optimum, reasonably fast.

We have indications¹⁴ that minimization of t_f while satisfying the end-point (product) constraints on x_m and μ_n , leads to a simultaneous minimization of the final value of the polydispersity index (PDI) as well (which is also required for having a product with desired physical properties), and so we need not incorporate the final value of the PDI in the optimization algorithm.

EXPERIMENTAL

A brief description of the experimental details are provided here. A full description is available in our earlier papers.^{6,7,15}

Rheometer–reactor Assembly

The experimental system^{6,7,15} is shown schematically in Figure 1. The polymerization is carried out in the gap between the rotating stainless steel cup and the concentric, stationary bob (SV400, Haake® Mess-Technik GmbH, Germany) of a viscometer, so that the viscosity, $\eta(t)$, of the reaction mixture can be measured simultaneously. The Haake® viscometer was modified to take care of all the requirements for polymerization.^{6,7} Water at the appropriate temperature is circulated from a programmable Julabo® F10-MH (Julabo Labortechnik GmbH, Germany) circulating bath through a space provided in the specially de-

signed cup (see Figure 1b) so as to maintain the reaction mixture in the gap at the desired (set point) temperature history, $T_{\text{op}}(t)$ or $T_{\text{reop}}(t)$. The rheometer–reactor assembly sends signals to a measuring system (Haake® RV20) interfaced with a PC (Pentium, 133 MHz) over an RS-232 serial line through the rheocontroller (Haake® RC20). When run in the ‘rotation’ mode, the values of shear stress, τ , and shear rate, $\dot{\gamma}$, are recorded continuously with time and used to compute the viscosity, $\eta(t)$. The rheometer–reactor assembly has an arrangement to exclude oxygen from the reaction mass so that trustworthy results are obtained for polymerization as well as viscosity.⁷ A separate degassing unit serves as a feed-preparation vessel.

Calibration and Measurement of Viscosity

The rheometer–reactor assembly was calibrated prior to its use. Standard viscosity test fluids [E6000 ($\eta = 5 \text{ Pa s}$ at 20°C) and E40000 ($\eta = 43.3 \text{ Pa s}$ at 20°C)], supplied by Gebrueder Haake GmbH, Germany, were used for this purpose. Calibration procedures recommended by the manufacturer were followed. The measurement of torque at the beginning of the reaction was done at a shear rate of 10 s^{-1} . The shear rate was lowered to 2 s^{-1} when the viscosity of the reaction mixture reached $\sim 5\text{--}8 \text{ Pa s}$. When the viscosity of the reaction mixture attained a value of $\sim 85\text{--}90 \text{ Pa s}$ (onset of the gel-effect), the shear rate was further lowered to 0.1 s^{-1} . These procedures ensured that the values of viscosity were close to zero-shear values and were measurable. The measuring system got overloaded at viscosities of $> 26,000 \text{ Pa s}$, and the bob automatically stopped rotating to avoid damage to the system. The rotating bob also worked as a stirrer during the polymerization.

Materials

Purified LR grade MMA (Central Drug House, Mumbai, India) and the initiator, LR grade AIBN (SAS Chemicals, Mumbai, India), recrystallized from LR grade methanol (Ranbaxy Laboratories, S. A. S. Nagar, Punjab, India), were used. The purification procedures described in detail previously⁶ were followed.

On-line Optimizing Control

The desired amount of initiator was dissolved in 25 mL of purified MMA in the degassing unit.

Argon (IOLAR-I grade, Indian Oxygen Limited, New Delhi, India) was sparged into this mixture at a very slow rate for $\sim 20 \text{ min}$ to remove the dissolved oxygen, a reaction inhibitor. The pressure vessel (A in Figure 1a), in which the rheometer–reactor assembly is placed, was first flushed with argon to displace the air initially present. Then, the oxygen-free reaction mixture was transferred (by gravity) from the degassing unit directly into the annular gap of the rheometer–reactor assembly that was preheated to the desired (initial) temperature. Argon was then charged in the pressure vessel, and a pressure of $\sim 2.5 \text{ Kg/cm}^2$ gage was maintained inside to prevent vaporization of the monomer (and so avoid bubble formation in the reaction mixture in the annulus of the viscometer, thus providing correct values of the viscosity). The reaction mixture attained the desired initial temperature within 2–3 min. After this time, the off-line optimal temperature, $T_{\text{op}}(t)$, was provided as a set point trajectory to the circulating programmable bath. The latter, in turn, implemented it on the reaction mass using hot water at appropriate temperatures (using PI control). The exothermic heat generated later on, at the onset of the gel effect, was removed by circulating water at ambient temperature through the cup for a very short period of time when required. The temperature of the reaction mass was measured and recorded periodically with the help of a thermocouple dipped in the reaction mass (Figure 1). The calibration of the thermocouple was checked before every 2nd–4th run.

The optimal (set point) temperature history, $T_{\text{op}}(t)$, was computed off-line (prior to polymerization) using GA, by solving the following problem:

$$\min I_1(t)[T(t)] \equiv t_f \quad (2)$$

subject to (s.t.):

$$x_{\text{mf}} \equiv x_{\text{m}}(t = t_f) = x_{\text{md}} = 0.92 \quad (3)$$

$$\mu_{\text{nf}} \equiv \mu_{\text{n}}(t = t_f) = \mu_{\text{nd}} = 4200 \quad (4)$$

model equations:^{8,16}

$$d\mathbf{x}/dt = \mathbf{f}[\mathbf{x}, T(t)] \quad (5)$$

$$\mathbf{x}(t = 0) = \mathbf{x}_0 \quad (6)$$

$$50^\circ\text{C} \leq T(t) \leq 70^\circ\text{C}$$

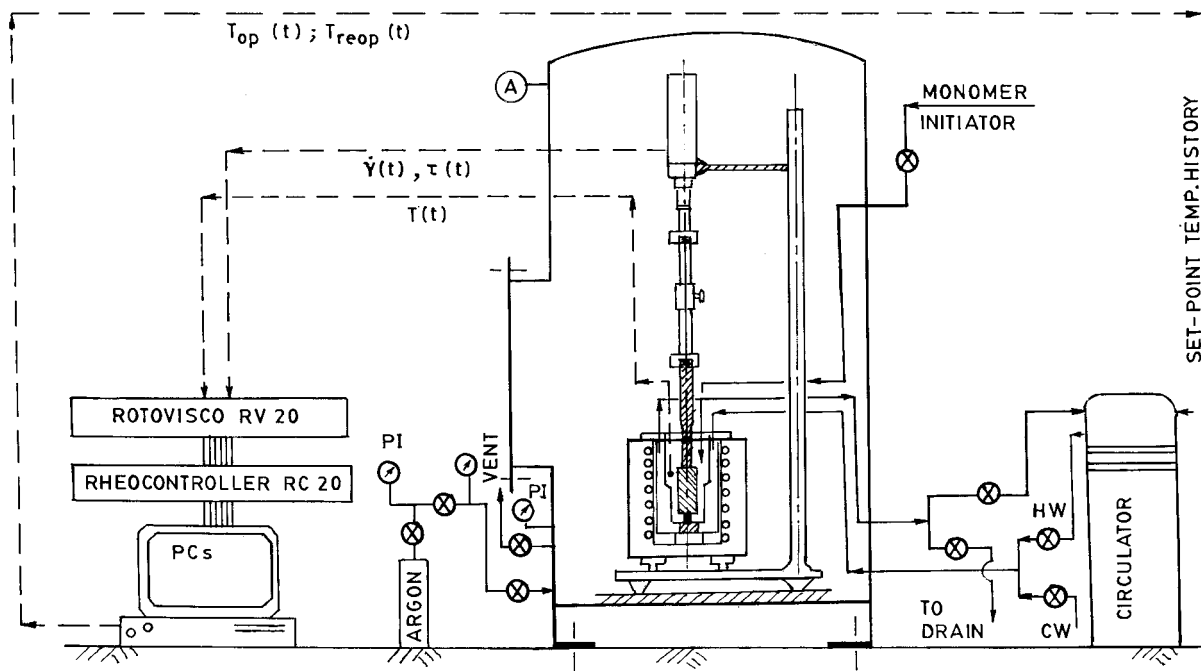


Figure 1 Schematic diagram of the (a) modified rheometer-reactor assembly, as used for on-line optimizing control, and (b) the cup and bob assembly.

In eqs. 2–6, I_1 is the objective function, \mathbf{x} is the vector of state variables,^{8,16} and \mathbf{x}_0 are the initial values (at $t = 0$) of \mathbf{x} . The computed optimal temperature history, in the form of an output file (digitized information), was provided directly (in the right format) as an input file to the Julabo® circulator control program, which implements it on the reaction mass using hot water at PI-controlled temperatures. The measured temperature history was found to lie within $\pm 0.5^\circ\text{C}$ of the set point (and so we do not distinguish the set point and the measured values). In other words, the tracking of the set point temperature history is excellent. The measured temperature history is continuously written (and updated) as an output file in the PC.

At some pre-decided time, t_1 , a planned disturbance (heater failure in this work) was introduced into the system by switching off the circulation of hot water through the cup, between the times t_1 and t_2 . The temperature of the reaction mass in the rheometer-reactor assembly falls slowly with time for $t_1 \leq t \leq t_2$. The rate of fall, R , of temperature is almost constant over time (for any experimental run), this rate being quite small because the system is well insulated. The rates of cooling are different for different runs because they were carried out on different days, and the experimen-

tal conditions at $t = t_1$ differed. It may be noted that the total fall in the temperature in time, $t_2 - t_1$, is small.

Five experimental runs were conducted with different heater failure conditions [different t_1 and t_2 , and so, different (*measured*) rates of cooling]. These experimental runs are indicated in this work by the symbol, $t_1 F(t_2 - t_1) R$. For example, the symbol 39F12, 0.64 indicates that the heating failure starts (t_1) at 39 min and lasts for 12 min ($t_2 - t_1 = 12$ min), during which time the *measured* cooling rate is $0.64^\circ\text{C}/\text{min}$. It is assumed that the fault in the heating system is (somewhat arbitrarily) rectified at $t_2 = 51$ min.

The on-line reoptimization of the temperature history takes t_{comp} (~ 2 min) of real time on a second PC, a Pentium II, 266 MHz. Hence, at time $t = t_2 - t_{\text{comp}}$, this computer code is started. The following reoptimization problem is solved to evaluate $T_{\text{reop}}(t)$:

$$\min I_2(t)[T_{\text{reop}}(t)] \equiv t_f^* - (t_2 - t_{\text{comp}}) \quad (7)$$

subject to (s.t.):

$$x_{\text{mf}} \equiv x_{\text{m}}(t = t_f^*) = x_{\text{md}} = 0.92 \quad (8)$$

$$\mu_{\text{nf}} \equiv \mu_{\text{n}}(t = t_f^*) = \mu_{\text{nd}} = 4200 \quad (9)$$

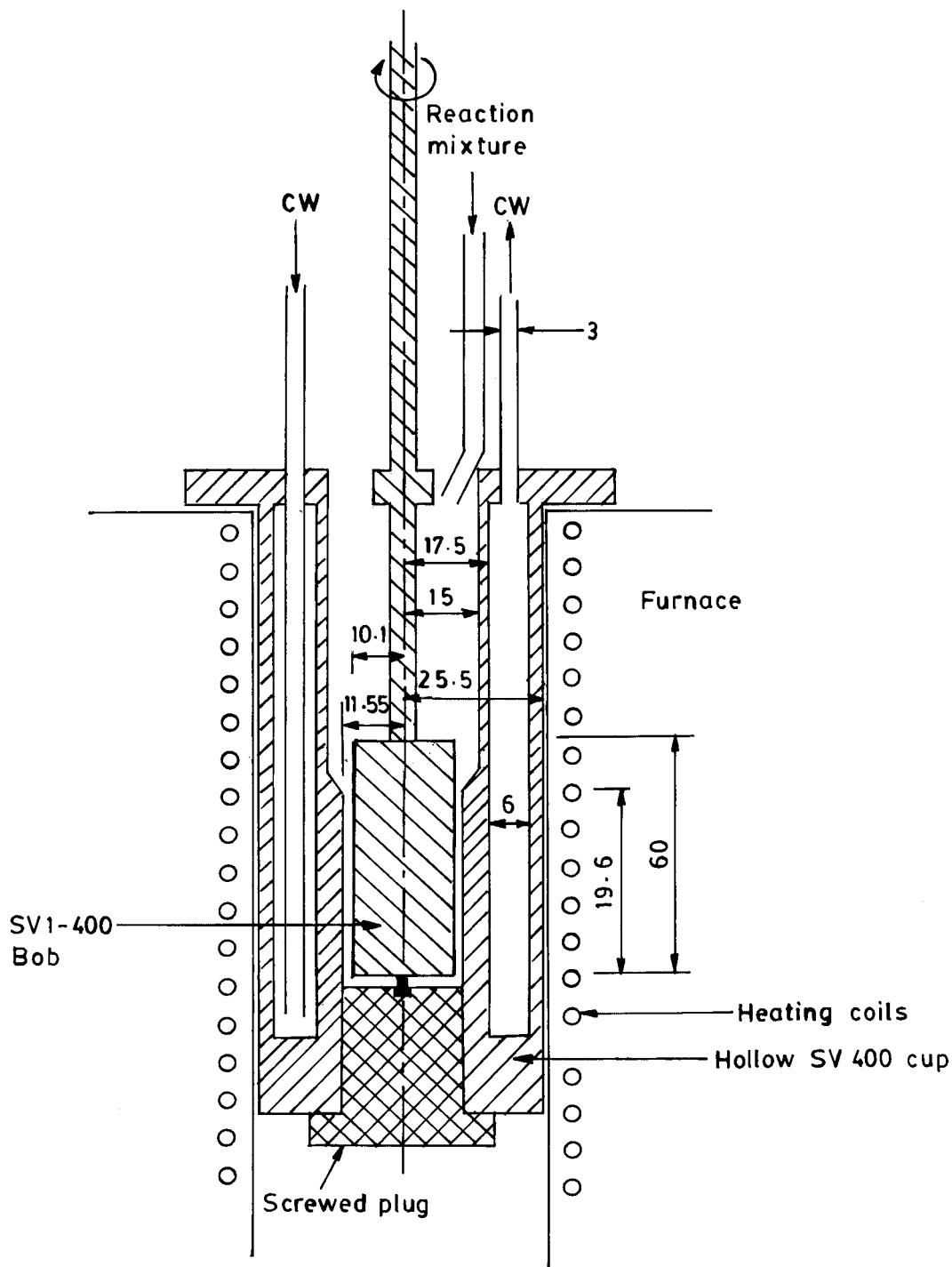


Figure 1 (Continued from the previous page)

model eqs.^{8,16}

$$d\mathbf{x}/dt = \mathbf{f}[\mathbf{x}, T(t)] \quad (10)$$

$$\mathbf{x}(t = t_2 - t_{\text{comp}}) \text{ continuous} \quad (11)$$

$$50^\circ\text{C} \leq T(t) \leq 70^\circ\text{C}$$

In eqs. 7–9, t_f^* is the new final (total) reaction time. The *experimental* temperature history is used (in the form of a 17th-order Chebyshev fit) in the model equations to generate the values of the concentrations and moments at t_2 minus t_{comp} . These values are then used as ‘initial’ conditions

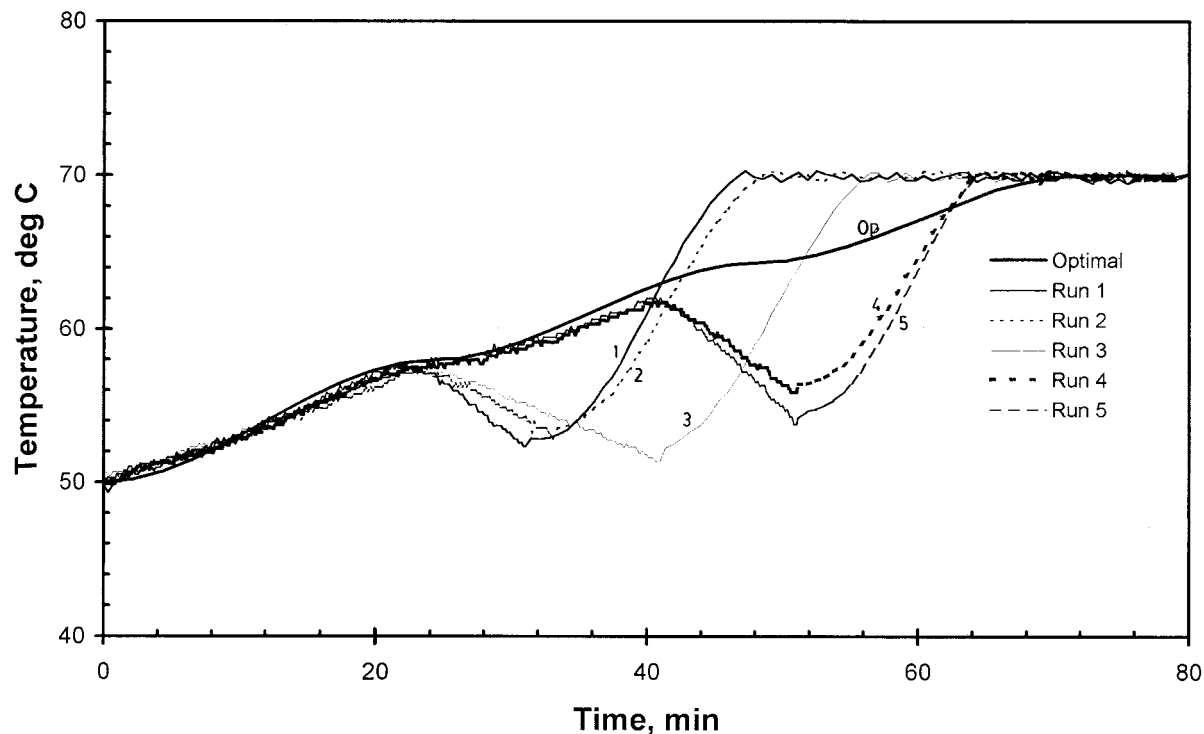


Figure 2 Experimental temperature histories for the six sets of experiments described in Table I. Values of t at which the bob stops rotating, are provided in Table I. T remains at 70°C beyond this point until $t = t_f^*$.

at $t = t_2 - t_{\text{comp}}$, in eqs. 7–11. The reoptimized temperature history is directly transferred as an input file (in the desired format) to the Julabo® circulator program. Again, the measured temperature history for $t \geq t_2$ was found to lie within 0.5°C of the desired set point, $T_{\text{reop}}(t)$. It may be mentioned here that prior knowledge of t_2 , when the heater starts to work again, is neither a ne-

cessity nor is lack of such knowledge a serious limitation because one can start running the reoptimization code soon after the heater failure is sensed ($|T_{\text{expt}} - T_{\text{op}}| \geq \text{a pre-assigned value}$), and check at the end of the optimization (after t_{comp} of ~ 2 min) if the fault is rectified. If the answer is in the affirmative, then the reoptimized temperature trajectory is transmitted to the Julabo® cir-

Table I Details of the Six Experimental Runs^a

Run Number	Code	t_f or t_f^* min (computed)	x_{mf} (computed)	μ_{nf} (computed)	Viscosity measurement stops at, min
Optimal temp history					
	T_{op}	91.9	0.902	4278	63.7
1	21F10, 0.45	97.5	0.891	4148	69.1
2	21F12, 0.32	99.3	0.896	4023	69.7
3	21F20, 0.30	102.2	0.890	4571	73.1
4	39F12, 0.48	116.2	0.903	4748	76.0
5	39F12, 0.64	123.7	0.911	4679	78.7

^a Best fit correlations (BFCs)¹⁶ used for θ_t , θ_p , θ_f . A 17th-order Chebyshev fit of the experimental temperature history is used for computing x_{m} and μ_{n} .

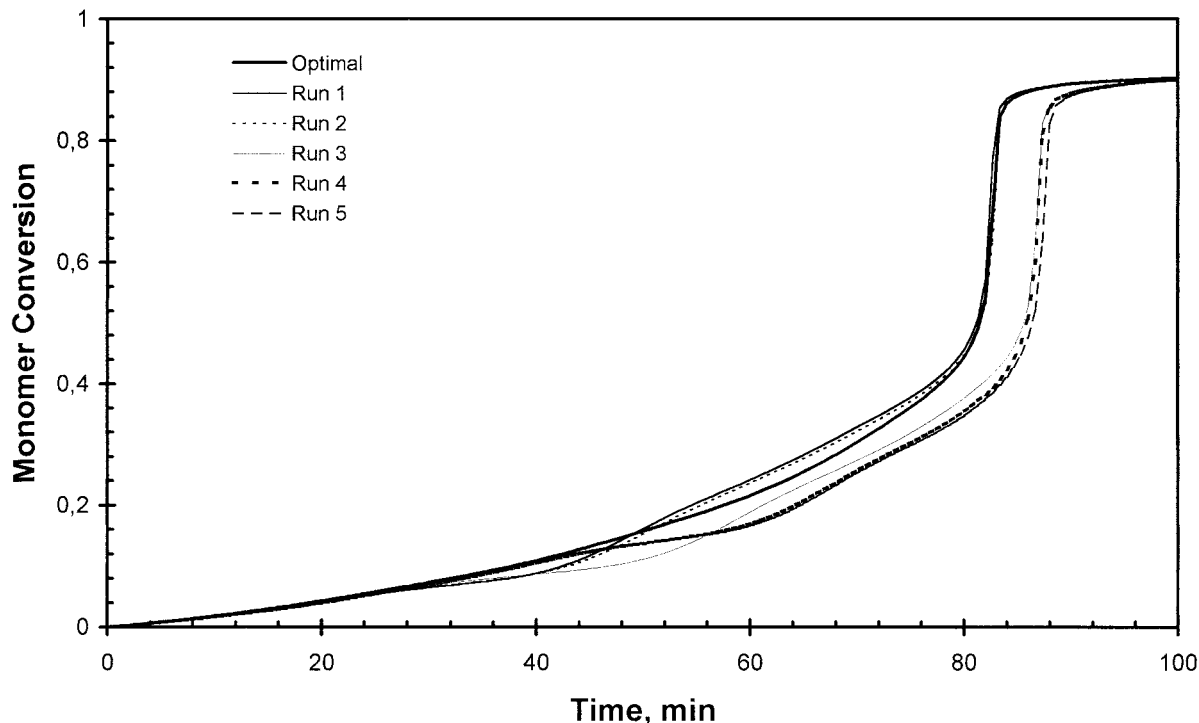


Figure 3 Model predictions for monomer conversion versus time for the six sets of experiments described in Table I. BFCs¹⁶ were used along with Chebyshev fits of experimental $T(t)$ to obtain the results. Results are shown until times t_f or $t_f^* I_o = 25.80 \text{ mol/m}^3$.

culator for implementation; otherwise, the reoptimization is repeated using the *updated* experimental temperature history.

At any time, the following four programs are run on the two PCs in different windows:

1. Viscosity measurement (Rotovisco Software) and recording
2. Temperature measurement and recording
3. Control (PI) program of the Julabo[®] circulator
4. Reoptimization (GA)

The mouse clicks the reoptimization program to execute it. The end of this computation can be observed in this window. When this happens, the mouse is used to click 'RUN' in the window for the control program of the Julabo[®] circulator (at $t = t_2$) to start it. In the present work, two PCs (Pentium[®] II, 266 MHz and Pentium 133 MHz) were used, the first performing the reoptimization and the second carrying out the other three sets of calculations already described. However, the aforementioned four computations can possibly be done on a single, faster PC.

It may be emphasized that $T_{\text{reop}}(t)$ is evaluated using information at $t = t_2 - t_{\text{comp}}$, and is implemented a little later, at $t = t_2$, when the temperature and the concentrations of all the species and the values of the several moments are slightly different. It is assumed that because t_{comp} is small, this does not lead to any significant errors.

To reduce the *real* time required to compute $T_{\text{reop}}(t)$, several changes were made in the values of the computational parameters of GA, from those used to compute $T_{\text{op}}(t)$ off-line.^{9,13} These changes are:

1. the chromosome length, N_{ga} , was reduced from the earlier value of 10 to 7;
2. the maximum number of generations, $N_{\text{g,max}}$, was reduced from 20 to 1–2 (this reduction was not found to be too critical);
3. the population size, N_{p} , was reduced from 100 to 20 (this change was found to be the most effective); and
4. the initial guess (estimate) of t_f^* was reduced from 16,000 to 10,800 s.

All these changes give a slightly less accurate $T_{\text{reop}}(t)$, but ensure that the computation of

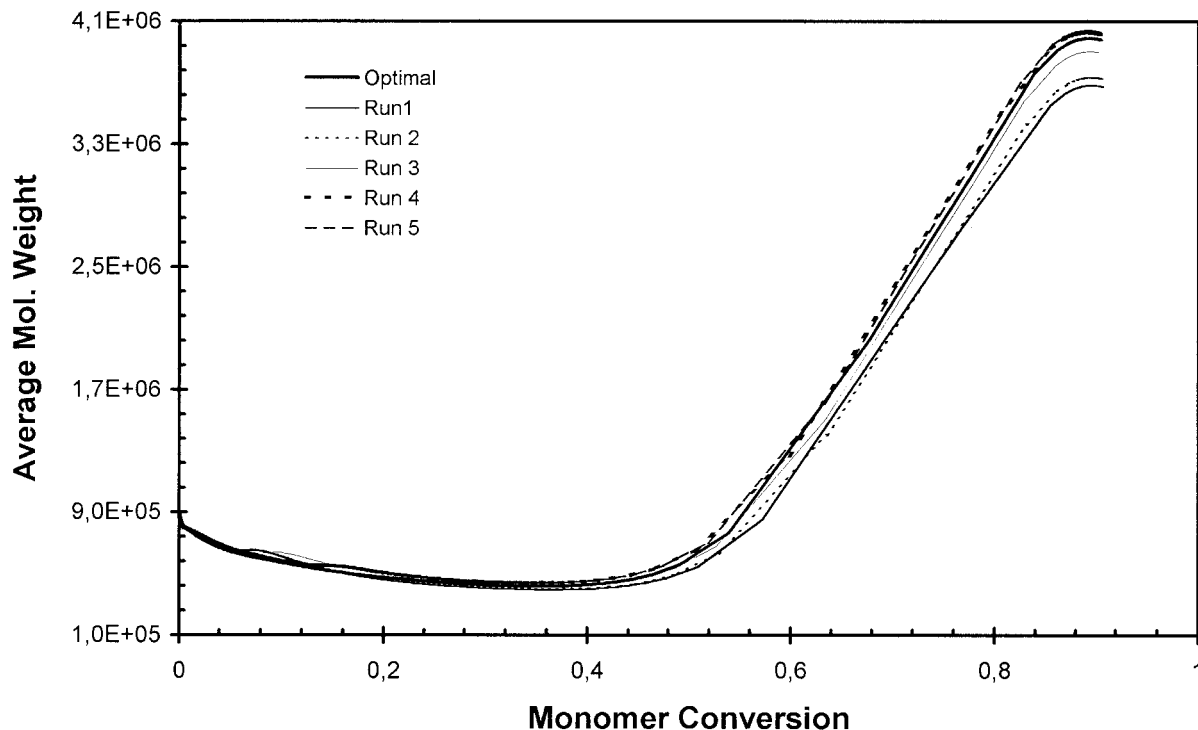


Figure 4 Model predictions for the weight average molecular weight versus monomer conversion for the six sets of experiments described in Table I. BFCs¹⁶ were used along with Chebyshev fits of experimental $T(t)$ to obtain the results. Results are shown until times t_f or $t_f^* I_0 = 25.80 \text{ mol/m}^3$.

$T_{\text{reop}}(t)$ can be completed in ~ 2 real min (102 s, to be precise).

RESULTS AND DISCUSSION

Bulk polymerization of MMA was carried out in the rheometer–reactor assembly with an initiator (AIBN) loading, I_0 , of 25.80 mol/m^3 . One experimental run was conducted without any heater failure (referred to as ‘optimal temp history’ in Figures 2–6); that is, using $T_{\text{op}}(t)$ for $0 \leq t \leq t_f$. Five additional runs (Runs 1–5), incorporating heater failure and reoptimization, were also carried out. In these runs, $T_{\text{op}}(t)$ was used for $0 \leq t \leq t_1$, and $T_{\text{reop}}(t)$ was used for $t_2 \leq t \leq t_f^*$. The six sets of measured temperature histories are shown in Figure 2. The details of t_1 , t_2 , and R , as well as the computed values of t_f^* (or t_f), x_{mf} , and μ_{nf} , for these six cases are shown in Table I. The model-predicted values of the monomer conversion, $x_m(t)$, and of $M_w(t)$, using the *experimental* temperature histories (which are close to, but not *exactly* the same as the computed reoptimized temperature histories) are shown in Figures 3

and 4. It may be noted that the end-point constraint is on the number-average chain length and not on M_w . The results in Table I indicate that the constraints on x_{mf} and μ_{nf} are met satisfactorily (considering the fact that the experimental and not the computed temperature histories are used to generate these values). The existing PI controller on the programmable Julabo® circulator bath was adequate to track the set point temperature history reasonably closely, to within $\pm 0.5^\circ\text{C}$.

The experimental data on the viscosity, $\eta(t)$, for the six different runs are shown in Figure 5. These results were replicable. The same data, using logarithmic scales for viscosity so that the values at smaller values of t can be read accurately, are shown in Figure 6. The experimental results on viscosity show some sudden jumps. These are observed when the shear rates are changed suddenly from 10 to 2 s^{-1} and from 2 to 0.1 s^{-1} (the bob stops and then starts rotating again at a new speed corresponding to the new value of the shear rate). The predicted values of $\eta(t)$ using the model with the experimental temperature histories are also shown in these figures.

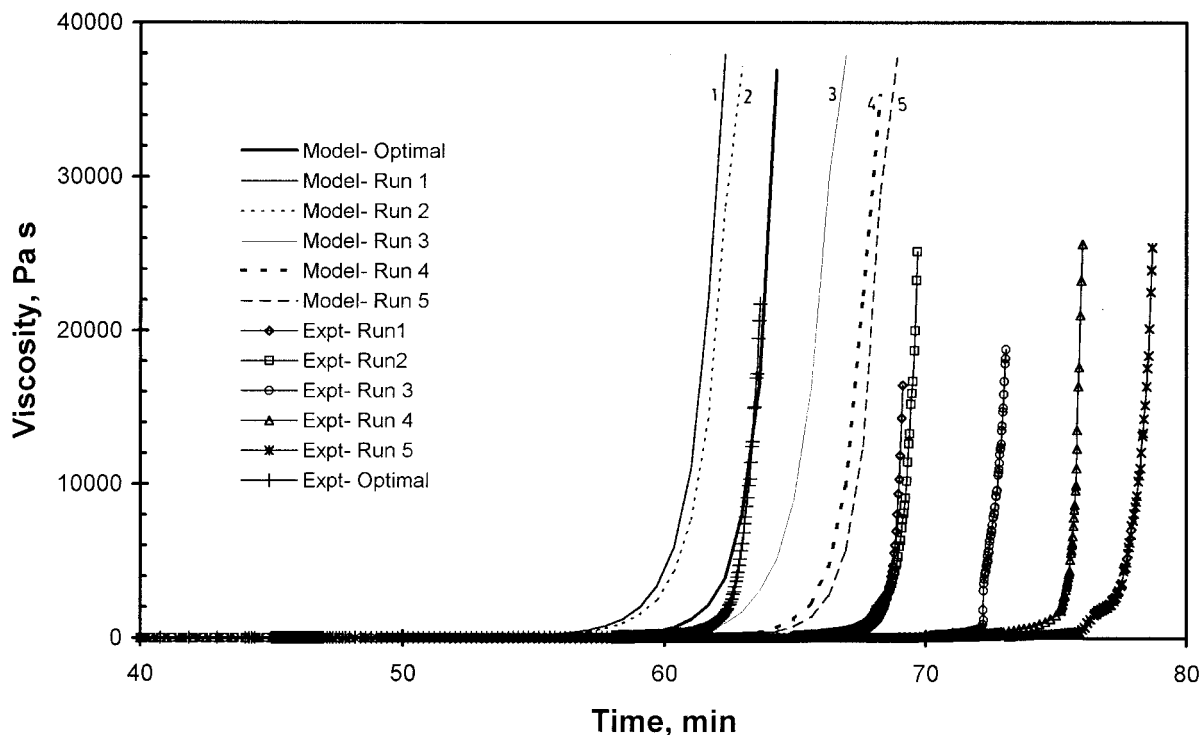


Figure 5 Comparison of experimental and model-predicted viscosities for the six sets of experiments described in Table I. The bob stops rotating soon after the last point shown on the experimental viscosity curve. $I_o = 25.80 \text{ mol/m}^3$. Model-predicted values of $x_m(t)$ (as in Figure 3) and $M_w(t)$ used with a linear interpolation of d_o-d_2 , to obtain model-predicted values of $\eta(t)$.

It is interesting to note from these figures that the agreement between the model-predicted and experimental values of viscosity for the case with no heater failure is excellent, as reported previously.⁷ In fact, it was this excellent agreement of the experimental $\eta(t)$ with the model-predicted values that suggested to us that model-based on-line optimizing control would be feasible for this system. The agreement between the experimental and model-predicted values of $\eta(t)$ for Runs 1–5 is not as satisfactory. It must be emphasized here that the experimental results [both $T(t)$ and $\eta(t)$] are replicable and trustworthy, and it is possible that it is the model that needs improvement. Indeed, it is well established⁸ that the present model is extremely sensitive to small changes in the values of the parameters characterizing the gel effect and more robust models for the diffusional effects associated with such polymerizations need to be developed. Moreover, for the case where there is no heater failure, the optimal temperature trajectory is monotonically increasing (almost linearly) from 50 to 70°C, and the agreement is satisfactory. In contrast, in the presence

of heater failure, the temperature rises initially ($t \leq t_1$), then falls ($t_1 \leq t \leq t_2$) and then rises again, finally reaching 70°C. It is conceivable that the viscosity correlation used here (values of d_o-d_2) breaks down because of temperature reversal, giving rise to the mismatch between experimental results and model predictions in Figures 5 and 6. This mismatch is particularly relevant because this viscosity correlation employs different constants for different ranges of temperature (and a linear interpolation of the constants is used). Further work is required (and is in progress) along these lines to settle the issue of this mismatch.

It is to be emphasized that very little experimental data are available in the open literature on the variation of viscosity with time for polymerizing systems, particularly under non-isothermal conditions. The data in Figures 5 and 6 provide *replicable* (and, we believe, trustworthy) experimental results under the temperature histories shown in Figure 2 (notwithstanding the mismatch between the model-predicted and experimental values of viscosity). These results

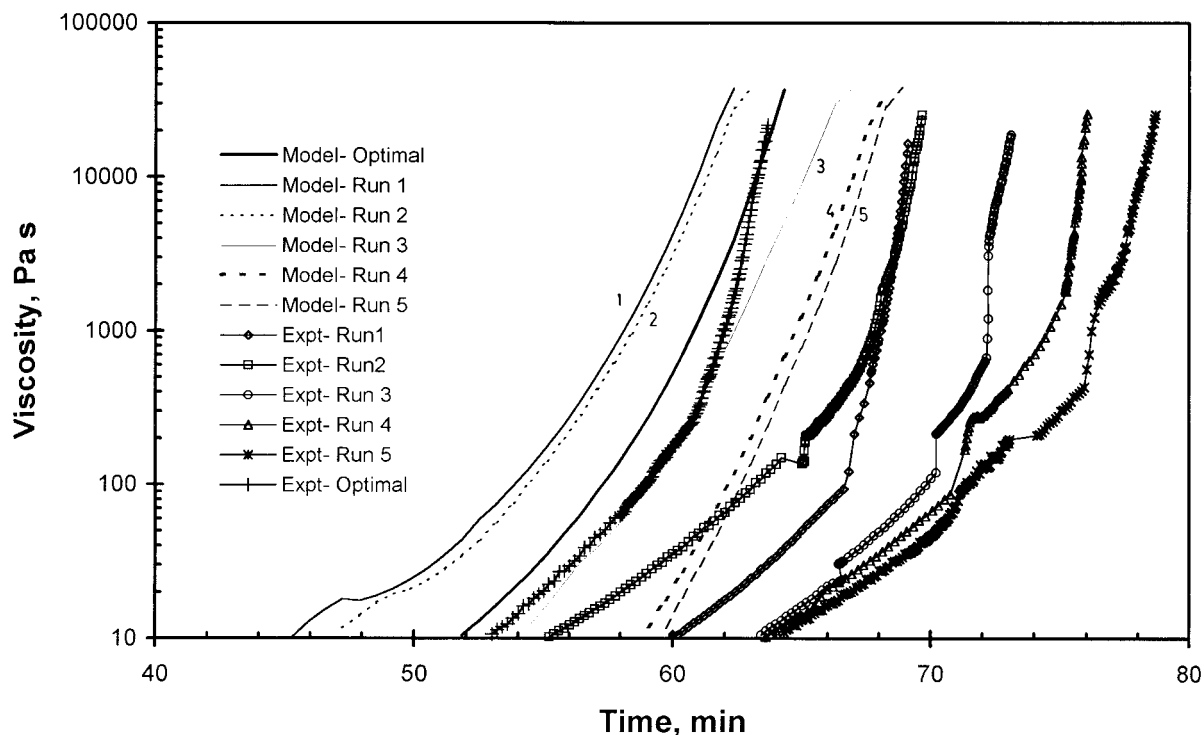


Figure 6 Comparison of experimental and model-predicted viscosities for the six sets of experiments described in Table I. Logarithmic scale for η used. $I_0 = 25.80 \text{ mol/m}^3$. Other details as for Figure 5

would be useful to other workers in the field in the development of better models.

CONCLUSIONS

Some experimental runs have been carried out on the on-line optimizing control of MMA polymerizations, using temperature and viscosity measurements for model-based inferential state estimation. A planned disturbance, namely, heating system failure during $t_1 \leq t \leq t_2$, was introduced experimentally in a rheometer-reactor assembly in which polymerization is taking place, under an off-line computed optimal temperature history. The optimal temperature history required to 'save the batch' after the disturbance, is re-computed on-line and implemented for $t > t_2$. The experimental histories of viscosity are replicable but are only in approximate agreement with model-predicted values, perhaps because the model is highly sensitive to the values of the parameters. A more robust model needs to be developed for this purpose. The experimental viscosity histories for six sets of non-isothermal conditions are trust-

worthy and can, indeed, be used for model development and tuning.

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NOMENCLATURE

c_{polym}	concentration of polymer (kg m^{-3})
d_0-d_2	coefficients in the viscosity equation (eq.1)
I_0	concentration of initiator at $t = 0$ (mol m^{-3})
M	total moles of monomer at time t (mol)
M_w	weight average molecular weight [$\equiv (MW_m)(\lambda_2 + \mu_2)/(\lambda_1 + \mu_1)$] (kg mol^{-1})
$T(t)$	temperature of the reaction mixture at time t (K or $^{\circ}\text{C}$)
t	time (min)
$x_m(t)$	monomer conversion (molar) at time t [$\equiv 1 - (M/\zeta_{m1})$]

Greek Letters

$\dot{\gamma}$	shear rate at time t (s^{-1})
η	viscosity of the reaction mass at time, t (Pa s)
η_{int}	intrinsic viscosity at reference temperature ($\text{m}^3 \text{kg}^{-1}$)
η_{sol}	solvent (monomer) viscosity (Pa s)
τ	shear stress (Pa)

Subscripts/Superscripts

d	desired value
expt	experimental
f	final value
op	optimal values (off-line computed)
reop	reoptimized values (on-line computed)

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