# Software Sensor for the Bulk Polymerization of Systems Exhibiting the Trommsdorff Effect Using Viscosity Measurements

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ABSTRACT: A model-predictive software sensor was developed for on-line estimation of monomer conversion and average molecular weight during bulk polymerization of systems exhibiting a gel effect. The viscosity and temperature of the reaction mass are the measured secondary variables, which when used with the model allow the state of the system to be estimated. The viscometer-reactor assembly was modified so as to measure the viscosity of the reaction mass during bulk polymerization of methyl methacrylate (MMA) at temperatures higher than those reported in our earlier work (Mankar, R. B.; Saraf, D. N.; Gupta, S. K. Ind Eng Chem Res 1998, 37, 2436).The viscosity data were curve-fitted using the modified Martin equation. Optimal temperature histories were then computed off-line, using a genetic algorithm, and implemented on the viscometer-reactor assembly in which the bulk MMA polymerization was carried out. The fact that the model tuned with the data obtained under the isothermal reactor operation can be used to predict the viscosity for nonisothermal (optimal or otherwise) reactor conditions without further tuning establishes the efficacy of the software sensor. This study can now be extended to investigate, experimentally, the on-line optimizing control of bulk MMA polymerizations. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2309-2326, 1999

**Key words:** software sensor; state estimation; bulk polymerizations; optimization; genetic algorithm; viscosity

#### INTRODUCTION

In the polymerization industry, there is a considerable economic incentive to develop real-time optimal operating policies that will result in the production of polymers with the desired molecular properties. The physical properties of any polymer depend largely on its average molecular weight and molecular weight distribution (MWD). Generally, from an applications point of view, it is desirable to have a high weight-average molecular weight,  $M_w$ , product with a narrow MWD. Martin et al.<sup>1</sup> and Nunes et al.<sup>2</sup> showed that narrowing the MWD improves the thermal properties, stress-strain relationships, impact resistance, hardness, and strength of the polymer. To produce such materials in industrial polymerization reactors, we must have appropriate (optimal) operating conditions. Several studies have been reported on the optimization of polymerization reactors, and these were reviewed by Farber,<sup>3</sup> Chakravarthy et al.,<sup>4</sup> and Mitra et al.<sup>5</sup> Very few

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experimental studies have been reported in the open literature on the control of free-radical bulk polymerization reactors, although several workers have reported work on the control of solution polymerization reactors. Soroush and Kravaris<sup>6</sup> implemented a scheme which tracked a specified optimal temperature history (computed off-line) in a solution polymerization [poly(methyl methacrylate) (PMMA)] batch reactor using a nonlinear (globally linearizing) control. Ellis et al.<sup>7</sup> used on-line size-exclusion chromatography to measure the MWD in an experimental reactor in which solution polymerization of methyl methacrylate (MMA) was carried out. Temperature or monomer addition alone and simultaneous temperature and monomer addition were used as manipulated variables to achieve a product having a specified weight-average molecular weight. Several workers<sup>8,9</sup> used a similar scheme in a batchsolution MMA polymerization reactor and showed that the reactor can be better controlled with an on-line state estimator. These studies were carried out under experimental conditions wherein diffusional limitations are not manifested.

The control of polymerization reactors in the presence of severe diffusional limitations (as in *bulk* polymerizations) is expected to pose a formidable challenge, since these reactors are associated with an extremely fast increase in the monomer conversion,  $x_m$ , with time, t, after the onset of the gel or Trommsdorff effect.<sup>10,11</sup> Such rapid changes in  $x_m(t)$  leave almost no choice to the control engineer except to use models having excellent predictive capabilities. Model-based control is, thus, essential for the proper control of such reactors,<sup>12</sup> since, often, one has to take control action (such as changing the temperature) much before diffusional effects manifest themselves. Several theoretical studies have been reported on developing model-based control strategies for polymerizations exhibiting diffusional limitations, as, for example, the recent works of Scali et al.<sup>13</sup> and Crowley and Choi.<sup>14</sup> The control of free-radical bulk polymerization reactors poses yet another problem, namely, the lack of suitable measuring instruments which can be used online.<sup>15</sup> Chien and Penlidis<sup>16</sup> presented an extensive review of on-line sensors for polymerization reactors. The use of gel permeation chromatography/HPLC to obtain the MWD, as well as the use of available densitometers for estimating monomer conversion, is limited to solution polymerizations, and these cannot be used easily for bulk polymerizations. In our earlier article,<sup>17</sup> the use

of experimental data on the viscosity,  $\eta(t)$ , of the reaction mass and its temperature, T(t), as a state estimator (software sensor) was demonstrated. The feasibility of such a model-based inferentialstate estimation technique was studied using pseudo (theoretically generated) experimental data.<sup>18</sup> This study showed that the state of the system  $(x_m \text{ and } M_w)$  can be predicted *uniquely* using  $\eta(t)$  and T(t) with a model. More recently, Garg et al.<sup>19</sup> demonstrated theoretically that such a software sensor can be used for on-line optimizing control of bulk polymerization reactors and that corrective action (reoptimize temperature history) can be taken to save the batch after equipment failures are sensed. For such a model-based inferential state estimation, one needs, in addition to a good model for the reactor, an equation relating  $\eta(t)$  and T(t) to  $x_m$  and  $M_w$ . This is one of the problems studied in this work.

Another important problem discussed here is the computation of an optimal temperature history and its implementation on a viscometer-reactor assembly developed in our laboratory. A commonly studied optimization problem<sup>4,20,21</sup> is to obtain the temperature history (the control variable) which minimizes the total reaction time,  $t_{f}$ , while simultaneously requiring the final monomer conversion,  $x_{mf}$ , and the final value of the number-average chain length,  $\mu_{nf}$ , to meet certain specifications (referred to as desired values,  $x_{md}$ and  $\mu_{nd}$ ). This ensures economic operation as well as product property requirements and is referred to as the minimum time problem. Another important optimization problem studied in the literature is the minimum polydispersity index (PDI) problem, in which the PDI of the polymer product is minimized while satisfying constraints on  $x_{mf}$ and  $\mu_{nf}$ . We have some *recent* indications<sup>4,22</sup> that the minimization of  $t_f$  while satisfying constraints on  $x_{\rm mf}$  and  $\mu_{\rm nf}$  leads to a simultaneous minimization of the final value of the PDI as well. Hence, we need to study the first (minimum-time) problem only. The genetic algorithm  $(GA)^{23,24}$  was used in this work to compute optimal temperature histories (off-line), which can then be implemented experimentally. The GA is a robust technique and gives solutions reasonably fast which are quite close to the global optimum. Because of its speed, the GA is much better suited for on-line optimization work than are earlier techniques (like Pontryagin's minimum principle). Indeed, Lee et al.<sup>21</sup> demonstrated *theoretically* that use of a few heuristic rules with the GA could be quite effective in the optimal operation of a continuous copolymerization reactor.

In this article, we first present some (additional) experimental data on the viscosity of the reaction mass as a function of time during bulk polymerization of MMA under isothermal conditions at 70°C. These data, along with data from our earlier work<sup>17</sup> at (isothermal) 50 and 60°C, were used to develop correlations for the parameters in a semiempirical equation for viscosity. We then present some work on the implementation of an optimal temperature history (computed off-line) on a viscometer-reactor assembly. This equation has been subsequently used to predict viscosity for nonisothermal systems (between 50 and 70°C) where the temperature history may or may not be optimal, without further tuning of the parameters. Experimental results obtained indicate that the model (equation for viscosity and the kinetic model) developed herein is quite good and can be used with confidence for future studies in on-line optimizing control of bulk MMA polymerizations. The techniques and methodologies developed are quite general and can easily be applied to other polymerizations requiring model-based predictive control.

# COMPUTATION OF OFF-LINE OPTIMAL TEMPERATURE HISTORY

Most of the earlier work on the optimization of polymerization reactors used Pontryagin's minimum principle or a constrained pattern search technique to solve a variety of optimization problems. These were described by Farber.<sup>3</sup> The GA is an extremely powerful search technique based on the mechanics of natural genetics and natural selection. This algorithm was introduced by Holland.<sup>23</sup> It involves a random search over the control variable domain after the problem has been appropriately coded, usually in terms of strings or chromosomes comprising binary numbers. The best few solutions evolve over generations using techniques which mimic genetic evolution. This technique has been proved to be very efficient, especially in cases where the objective function is flat and exhibits several local optima.<sup>24</sup> The advantage of the GA lies in the fact that it works without requiring much information about the system, in contrast to the traditional techniques which need gradients, initial guesses, etc. Hence, for more complex systems where the gradients cannot be easily evaluated and a reasonable ini-

# Table IKinetic Scheme for Free-radicalPolymerizations

Initiation	$\stackrel{(f)k_d}{I \longrightarrow} 2R$		
	$R + M \xrightarrow{k_i} P_1$		
Propagation	$P_n + M \xrightarrow{k_p} P_{n+1}$		
Termination by combination	$P_n + P_m \xrightarrow{k_{tC}} D_{n+m}$		
Termination by disproportionation	$P_n + P_m \xrightarrow{k_{td}} D_n + D_m$		

 $k_{tc} \approx 0$  for MMA polymerization.

tial guess is not available, the GA leads to solutions which are very close to the global optimum. In this work, we apply the GA to obtain (off-line) optimal temperature histories for bulk MMA polymerizations.

Table I shows the kinetic scheme characterizing several important free-radical polymerizations [e.g., PMMA, polystyrene (PS), poly(vinyl chloride) (PVA), etc.]. Mass balance and moment equations for MMA polymerization in a semibatch reactor are given by equations<sup>25</sup> having the general form

$$d\mathbf{x}/dt = \mathbf{F}(\mathbf{x}, \mathbf{u}); \quad \mathbf{x}(t=0) = \mathbf{x}_0 \tag{1}$$

where  $\mathbf{x}(t)$  is the vector of state variables defined by

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

and  $\mathbf{u}(t)$  is the vector of control variables [in the present case, it is a scalar, T(t)]:

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

 $\lambda_k$  and  $\mu_k$  (k = 0, 1, 2, ...) represent the *k*th moments of the chain-length distributions of species  $P_n$  and  $D_n$ , respectively.  $\zeta_m$  and  $\zeta_{m1}$  are additional variables to account for the addition and vaporization of the monomer after time t = 0 and are useful in the definition of the monomer con-

version,  $x_m$ , for semibatch reactors. The other symbols are defined in the Nomenclature. The exact equations [functions, F, in eq. (1)] and the values of the several properties and parameters used for MMA polymerization are available elsewhere<sup>26</sup> and are not repeated here for the sake of brevity.

The rate constants,  $k_{td}$  and  $k_p$ , and the initiator efficiency, f, in Table I become diffusion controlled as the polymerization progresses. The exact form of these kinetic "constants" is given by

$$\frac{1}{k_{td}} = \frac{1}{k_{td,0}} + \theta_t(T)\mu_n^2 \frac{\lambda_0}{V_l \exp[-\psi + \psi_{ref}]}$$
(4a)

$$\frac{1}{k_p} = \frac{1}{k_{p,0}} + \theta_p(T) \frac{\lambda_0}{V_l \exp[\xi_{13}\{-\psi + \psi_{\text{ref}}\}]} \quad (4b)$$

$$\frac{1}{f} = \frac{1}{f_0} \left( 1 + \theta_f(T) \frac{M}{V_l \exp[\xi_{I3}\{-\psi + \psi_{\text{ref}}\}]} \right) \quad (4c)$$

The model parameters are

$$\mathbf{p} = [\theta_t, \ \theta_p, \ \theta_f]^T \tag{5}$$

The model parameters were calculated for the individual temperatures using a curve-fit of the isothermal data on  $x_m(t)$  of Balke and Hamielec<sup>27</sup> on MMA polymerization in small ampules as well as those of Mankar et al.<sup>17</sup> in the viscometer-reactor assembly. For nonisothermal situations, the best-fit correlations of Seth and Gupta<sup>25</sup> were used.

The kinetic model was used in this study to minimize the following (single) objective function:

Min 
$$I[u(t)] = t_f + w_1(1 - x_{mf}/x_{md})^2$$
  
+  $w_2(1 - \mu_{nf}/\mu_{nd})^2$  (6a)

subject to

$$dx/dt = \mathbf{F}(x, u); \quad \mathbf{x}(t=0) = \mathbf{x}_0$$
 (6b)

$$u_{\min} \le u(t) \le u_{\max} \tag{6c}$$

In eq. (6),  $w_1$  and  $w_2$  are (large) weighting factors used as two penalty functions incorporated into the objective function *I*. The choice of the objective function in eq. (6) minimizes the deviations (due to large values of  $w_1$  and  $w_2$ ) of  $x_{\rm mf}$  and  $\mu_{\rm nf}$  from their desired values while simultaneously minimizing  $t_f$ . The choice,  $x_{mf} \cong x_{md}$ , forces the amount of the unreacted monomer to be small, thus keeping postreactor separation and recycling costs low. The choice,  $\mu_{nf} \cong \mu_{nd}$ , forces the polymer properties to be as per specifications since several physical properties of polymers are related to the value of their  $\mu_n$ . The objective function in eq. (6) was used earlier by Sachs et al.<sup>20</sup> but with a different kinetic model. The initial values,  $\boldsymbol{x}_0$ , in eq. (1) are given by

where  $I_0$  and  $M_0$  are the initial values of the initiator and monomer concentrations, respectively.

The GA was used to obtain the optimal temperature history for this problem. Additional details were provided in Chakravarthy et al.<sup>4</sup> Monomer conversion and weight-average molecular weight were computed for different isothermal conditions. These results were generated using an integration scheme (code DO2EJF) from the NAG FORTRAN library. The tolerance parameter, TOL, was assigned a value of  $10^{-7}$  and no significant differences were found upon decreasing the value of this parameter. This check indicated that the simulation part of our code was free of errors and also provided results which could be used to explain optimal histories qualitatively. The checks on the correctness of the optimization part of our program were made using the procedures and parameter values used by Chakravarthy et al.<sup>4</sup> The optimization program was run for

$$x_{\rm md} = 0.92$$
  
 $\mu_{\rm nd} = 4200$   
 $50^{\circ}{
m C} \le T(t) \le 70^{\circ}{
m C}$  (8)

with values of **p** as given by Seth and Gupta.<sup>25</sup> The choice of the above values was based on physical limitations of the viscometer-reactor assembly, on which the computed optimal temperature history was to be implemented. The optimal temperature history was obtained for this constrained optimization problem using maximum changes in the temperature *at any stage* of  $\pm 10^{\circ}$ C. This ensures that the computed temperature histories are physically realizable. Values of  $x_m(t)$  and  $M_w(t)$  were also computed under optimal conditions.



Figure 1 Schematic diagram of the modified viscometer-reactor assembly.

### **EXPERIMENTAL SYSTEM**

The experimental system developed earlier<sup>17</sup> was modified to prevent vaporization of the monomer at higher temperatures and is shown schematically in Figure 1. The viscometer-reactor assembly was placed in a pressure vessel. This was necessary because it was observed in our earlier study that beyond a temperature of about 62°C vaporization became significant and bubble formation started. These bubbles become entrapped in the reaction mass at high viscosities and led to significant fluctuations in the viscosity data. A stainless-steel bob (SV400, Haake Mess-Technik GmbH, Germany) was used for the measurement of the viscosity. To remove the exothermic heat generated, a stainlesssteel viscometer cup with a cooling jacket was fabricated and used. The internal dimensions of this cup were the same as those for the SV400 cup. Heat removal was achieved by circulating water at ambient temperature through this jacket when required. Hot water at an appropriate temperature was circulated through the jacket inside the viscometer cup to implement the desired optimal temperature history. The water was taken from a programmable Julabo F10-MH (Julabo Labortechnik GmbH, Germany) circulating constant temperature bath. In the previous study, electrical heating was used to raise the temperature of the reaction mass to the desired value. However, in the present work,

electrical heating was replaced by heating with hot water through the jacket. This management was preferred over the electrical heating because it facilitated implementation of the variable optimal temperature history as the bath was programmable. The setup is equipped with a separate degassing unit which also serves as a feed vessel for the reaction mixture. The viscometer-reactor assembly sends signals to a measuring system (Haake RV20) interfaced with a PC 486 over an RS-232 serial line through the rheocontroller (Haake RC20). The viscosity of the reaction mass is measured at the desired sampling times. The computer records the values of the shear stress,  $\tau$ , and the shear rate,  $\gamma$ , which, in turn, are used to calculate the viscosity of the reaction mass as a function of time. The viscometer-reactor assembly enables polymerization to be carried out in the annular gap between the cup and bob under almost any desired temperature history, while simultaneously measuring the viscosity online.

## CALIBRATION OF VISCOMETER-REACTOR ASSEMBLY

The viscometer-reactor assembly was calibrated prior to its use. Standard viscosity test fluids [E6000 ( $\eta = 5$  Pa s) and E40000 ( $\eta = 43.3$  Pa s) at 20°C], supplied by Gebrueder Haake GmbH, Ger-

many, were used for this purpose. The viscosity test fluid was filled in the cup and its temperature was lowered to  $20^{\circ}$ C ( $\pm 0.2^{\circ}$ C) and maintained thereafter by circulating cold water from a Julabo bath. The rheocontroller was set in the "rotation" mode, and by following the standard procedures described in the operating manual, calibration factors were determined.

# PURIFICATION OF MONOMER AND INITIATOR

LR-grade MMA (Central Drug House, Mumbai, India) was purified prior to use. The monomer was washed three times with equal volumes of a 5% sodium hydroxide (E. Merck, Mumbai, India) solution in double-distilled water to remove the phenolic stabilizers [quinol (hydroquinone), 0.01%] present in it. The mixture was allowed to settle in a separating funnel forming two layers; the bottom inorganic layer was discarded leaving the monomer. Traces of sodium hydroxide were removed from the treated monomer by washing it thrice with double-distilled water. Settling times of at least 2 h after each NaOH and water wash were allowed. The residual water was removed from the monomer by passing through beds of silica gel (mesh 3-8, NICE, Kochi, India) and molecular sieves (type 30-541, Linde Division, Union Carbide, Danbury, CT). Fresh batches of regenerated silica gel and molecular sieves (by washing and drying in an oven at about 70°C for 5 h and stored in air-tight containers) were used for every 250-mL batch of monomer. The monomer thus obtained was distilled under a vacuum  $(\approx 50 \text{ mmHg})$  at about 30°C. Ice-cold water was circulated in the condenser. A few beads of molecular sieves were added to a distillation flask to augment flashing of the monomer under a vacuum. The distilled monomer was kept in a refrigerator. The final yield of the monomer was about 60% of the original volume.

The initiator, LR-grade 2, 2'- azoisobutyronitrile (AIBN; SAS Chemicals, Mumbai, India) was recrystallized from LR-grade methanol (Ranbaxy Laboratories, S. A. S. Nagar, Punjab, India). A saturated solution of AIBN was prepared (at room temperature) in a conical flask. The solution was filtered using ordinary filter paper. The filtrate was chilled in a refrigerator to crystallize the AIBN. The crystals were recovered by filtration and dried in an oven under a vacuum at room temperature to avoid thermal decomposition. The mother liquor was stored for future use. The procedures followed are well documented in the literature.<sup>27,28</sup>

#### EXPERIMENTAL PROCEDURE

The desired amount of the initiator was dissolved in 25 mL of purified MMA and this reaction mixture was taken in the degassing unit. Argon (IO-LAR-I grade, Indian Oxygen Limited, New Delhi, India) was sparged at a very slow rate for about 20 min to remove the dissolved oxygen (a reaction inhibitor). The pressure vessel in which the viscometer-reactor assembly was placed was first flushed with argon to displace the air initially present. The pressure vessel was not evacuated to a high vacuum which could damage the viscometer head. Then, the oxygen-free reaction mixture was transferred (by gravity) from the degassing unit directly into the annular gap of the viscometer-reactor assembly preheated to the desired initial temperature. Argon was then charged in the pressure vessel and a pressure of around 2.5 kg/cm<sup>2</sup> was maintained until the end of the run. Visual inspection of the polymer in the viscometer gap at the end of polymerization confirmed the absence of bubbles. The reaction mixture attained the desired initial temperature within 2-3 min, after which a desired set-point temperature history (within an error of approximately  $\pm 0.5^{\circ}$ C) was implemented using the circulating hot water. The desired values of percentage heating rates (to be provided along with the set-point temperature to the Julabo circulator control program) were obtained by conducting several blank runs using water in place of the reaction mass. These are shown in Figure 2. It may be mentioned here that these heating rates are valid for the conditions under which these are determined, namely, ambient temperature ( $\approx 35^{\circ}$  C), the capacitance of the cooling jacket, and the tubing used.

The exothermic heat generated at the onset of the gel effect was removed by circulating water at ambient temperature through the jacket in the cup for a very short period of time around that period. No further cooling was required until the end of the run. Torque measurements were started at a shear rate of  $10 \text{ s}^{-1}$ . The shear rate was lowered to  $2 \text{ s}^{-1}$  when the viscosity of the reaction mixture reached about 5–8 Pa s. When the viscosity of the reaction mixture attained a value of about 85–90 Pa s (onset of the gel effect), the shear rate was further lowered to  $0.1 \text{ s}^{-1}$ .



**Figure 2** Optimal temperature histories (set-point and experimental) for two values of  $I_0$ .  $x_{\rm md} = 0.92$  and  $\mu_{\rm nd} = 4200$ . Water at ambient temperature (about 35°C) at an approximate flow rate of  $5 \times 10^{-3}$  m<sup>3</sup>/min was used during the cooling period indicated. Percent heating rates used are also shown.

These ensured that the values of the viscosity were close to the zero-shear values. The measuring system became overloaded above viscosities of about 26,000 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. The shear rate, shear stress, and temperature were recorded by the PC 486 as a function of time. The temperature of the reaction mass was measured with the help of a thermocouple placed in a thermowell which is dipped in the reaction mass (see Fig. 1). It was not possible to take out the samples from the viscometerreactor assembly (as was the case in our earlier work) as we were carrying out the reaction under pressure. Hence, we were not able to obtain experimental data on monomer conversions and weight-average molecular weights in the present study. However, experimental results on the viscosity under isothermal conditions obtained in the modified setup were close to those reported in our previous work (in which  $x_m$  and  $M_w$  were measured and found to be similar to values reported by Balke and Hamielec<sup>27</sup> in small glass ampules). This indicated that the experimental procedures were giving satisfactory results. It is important to note that after every test the cupand-bob were cleaned in LR-grade dichloromethane (NICE, Kochi, India). After reassembly, the cup-and-bob position was adjusted carefully to minimize friction. It was ensured that the inherent friction of the empty viscometer was always much less than that with the solution inside.

#### **RESULTS AND DISCUSSION**

Bulk polymerization of MMA was carried out in the viscometer-reactor assembly at two different initiator (AIBN) loadings ( $I_0 = 15.48$  and 25.80 mol/m<sup>3</sup>) at 70°C and also using two different optimal temperature histories (computed off-line and used as set points). The initiator loadings were the same as in the study of Balke and Hamielec<sup>27</sup> carried out under isothermal conditions in small glass ampules. Figure 2 also shows the temperature histories for both the experimental runs in which the off-line computed (using the GA) optimal temperature histories were tracked. It can be seen that the set-point temperature histories were well implemented. The temperature histories for the isothermal 70°C runs were quite similar to our previous work at 50 and 60°C and are not included here. A sample polymerization

run was made and it was confirmed that the experimentally measured values of the viscosity (measured *continuously* as its value increases) are indeed the "true" values (obtained using steady-state observations when the viscosity does not change over time; see Mankar et al.<sup>17</sup>). As the reaction proceeds, the reaction mixture becomes more and more viscous. The viscosity of the reaction mass increases dramatically after the onset of the gel effect, when  $x_m$  as well as  $M_w$  increase sharply. We were able to obtain several data points for the viscosity of the reaction mass using sampling periods (at which viscosities were recorded by the PC) between 6-10 s in this region. The sampling times employed in this study are smaller than those used in our previous study as the increase in viscosity in the gel-effect region is extremely fast compared to measurements at lower temperatures.

Figure 3 shows viscosity as a function of time for eight experimental runs (for the 50, 60, and 70°C and optimal cases at  $I_0 = 15.48$  and 25.80 mol/m<sup>3</sup>). The inset shows data in the low viscosity range. Values of viscosity below about 0.1 Pa s are untrustworthy since they go out of the range of the SV400 system. Several replicate runs were made to confirm reproducibility. It is to be noted that data on  $\eta(t)$  at 70°C are obtained only up to values of about 26,000 Pa s, while those at lower temperatures were obtained up to about 31,250 Pa s. This is because of the *extremely* sharp increase of viscosity with time. The viscometer slips (to avoid overloading) very shortly after the last sampling point, and in the short interval following this (during which data are not recorded), the viscosity would, indeed, have increased significantly to well above 31,250 Pa s.

The model predictions for  $x_m$  versus time for these optimal cases as well as for isothermal 50, 60, and 70°C, with  $I_0 = 15.48$  and 25.80 mol/m<sup>3</sup> are presented in Figure 4. The model predicted values of  $M_w$  plotted as a function of time are shown in Figure 5, whereas Figure 6 shows the model-predicted values of  $M_w$  plotted as a function of  $x_m$ . The values of  $x_m$  and  $M_w$  for the isothermal cases were generated using best-fit val*ues* of **p**. These were obtained for the *individual* isothermal cases using the Box complex nonlinear curve-fit procedure on all the available experimental data on  $x_m(t)$  of Balke and Hamielec<sup>27</sup> and also the experimental data from Mankar et al.<sup>17</sup> Values of these individually optimized parameters (IOPs) are given in Table II. It may be noted that the kinetic scheme adopted here consists of



**Figure 3** Experimental data on viscosity versus time for the eight cases studied. Data at 50 and 60°C (isothermal) are from Mankar et al.<sup>17</sup>  $T_{\rm opt}$  is in °C.



**Figure 4** Model predictions for monomer conversion versus time using the IOPs for the six isothermal runs and best-fit correlations (Seth and Gupta<sup>25</sup>) for the optimal cases. Points used for generating model-predicted values of viscosity (Fig. 9) are shown for the  $T_{\rm opt}$  (t) cases.



**Figure 5** Model-predictions for the weight average molecular weight *versus* time. Details as in Figure 4.

straightforward initiation, propagation, and termination steps. Chain-transfer reactions are unimportant for bulk polymerizations and are, hence, neglected. Figures 4 and 5 show that the two different initiator loadings used in this study lead to quite different conversion and molecular



**Figure 6** Model-predictions for the weight average molecular weight *versus* monomer conversion. Details as in Figure 4.

weight profiles at the same temperature, a higher initiator concentration resulting in a lower molecular weight. It can be seen that the limiting conversion at large values of times is lowest at 50°C and gradually increases with the polymerization temperature. This is consistent with the glass

$I_0 = 15.48 \text{ mol/m}^3$			$I_0 = 25.80 \text{ mol/m}^3$			
	50°C	60°C	70°C	50°C	60°C	70°C
$ \begin{array}{l} \theta_t \ (\mathbf{s}) \\ \theta_p \ (\mathbf{s}) \\ \theta_f \ \ (\mathbf{m}^3 \ \mathbf{mol}^{-1}) \end{array} $	$\begin{array}{l} 4.1397\times 10^{22} \\ 5.0266\times 10^{17} \\ 6.7632\times \ 10^{6} \end{array}$	$2.7689 imes10^{19}\ 9.0419 imes10^{14}\ 2.1861 imes10^{5}$	$4.74  imes 10^{16} \ 8.05  imes 10^{11} \ 2.86  imes \ 10^3$	$egin{array}{l} 4.7541  imes 10^{22} \ 3.1459  imes 10^{17} \ 2.1886  imes \ 10^7 \end{array}$	$egin{array}{l} 3.4970  imes 10^{19} \ 8.8996  imes 10^{14} \ 4.2918  imes \ 10^5 \end{array}$	$\begin{array}{c} 5.34\times10^{16}\\ 1.85\times10^{11}\\ 5.99\times10^{3}\end{array}$

Table II Individually Optimized Parameters (IPOs)

effect, whereby the reaction mixture essentially freezes at a composition whose  $T_{\rm g}$  corresponds to the reaction temperature. Also, increasing temperature at constant initiator loading significantly lowers the molecular weight. It is clear from Figure 6 that at high conversions, when the termination rate is greatly reduced, the weightaverage molecular weights increase appreciably. Another important feature characterizing the monomer conversion curves is the curvature of the conversion history before the onset of the socalled gel region. Onset of the gel effect is only a convenient phrase denoting the region of rapid rise in the conversion. There exists, in fact, no sharp demarcation in terms of molecular processes before and after the "occurrence" of this autoacceleration region. The rapid rise in conversion is merely a consequence of the increasing importance of mass-transfer limitations.

It is interesting to observe from Figure 2 that optimal operation requires relatively low temperatures in the initial stages (leading to high values of  $M_w$ ; see Fig. 5), followed by a gradual increase in T(t) associated with fall in  $M_w$ , to its maximum value of 70°C. The value of  $M_w$  (corresponding to desired  $\mu_n$ ) then builds up, exploiting the gel effect near the end of polymerization, this being exhibited as a sharp increase in  $M_w(t)$  and  $x_m(t)$  as seen in Figures 4–6, near  $t \approx t_{f}$ . This sudden increase in  $M_w$  is a characteristic of both the optimal temperature histories examined in this study. The temperature profile in the pre-gel-effect region is quite important, particularly since rapid changes in T(t) after the onset of the gel effect are not easy to implement experimentally. This emphasizes the need for model-based on-line optimizing control in the period prior to the onset of the gel effect.

The experimental data for  $\eta(t)$  for the six *iso-thermal* cases in Figure 3 are now used to develop appropriate correlations which can be used for estimating the state of the system using  $\eta(t)$  and T(t). The Martin equation<sup>29</sup> is

$$\ln \frac{\eta_{\rm sp}}{\eta_{\rm int} C_{\rm polym}} = K_M(\eta_{\rm int} C_{\rm polym}) \tag{9}$$

In eq. (9),  $\eta_{\rm int}$  is the intrinsic viscosity,  $\eta_{\rm sp}$  is the specific viscosity [=  $(\eta/\eta_{\rm sol})-1$ ], and  $C_{\rm polym}$  is the polymer concentration given by

$$C_{\rm polym} = (1 - \phi_m)\rho_p \tag{10}$$

$$\phi_m = \frac{(1 - x_m)/\rho_m}{(1 - x_m)/\rho_m + x_m/\rho_p}$$
(11)

where  $\phi_m$  is the volume fraction of monomer,  $\rho_p$  is the density of the pure polymer (1200 kg/m<sup>3</sup>), and  $\rho_m$  is the density of the pure monomer (kg/m<sup>3</sup>) at temperature *T* (K) given by (Baillagou and Soong<sup>30</sup>):

$$\rho_m = 966.5 - 1.1(T - 273.15) \tag{12}$$

In the definition of  $\eta_{\rm sp}$ ,  $\eta$  is the viscosity of the polymer solution and  $\eta_{\rm sol}$  is the viscosity of pure solvent (monomer in this case) in Pa s, given by (Yaws<sup>31</sup>):

$$\log_{10}\eta_{\rm sol} = A + B/T + CT + DT^2$$
 (13)

The values of the constants, A, B, C, and D (for MMA) are -7.7825,  $7.3478 \times 10^2$ ,  $1.0258 \times 10^{-2}$ , and  $-1.1343 \times 10^{-5}$ , respectively. The values of  $\eta_{\rm int}$  (dL/g) were calculated using the equation given by Cohn-Ginsberg et al.<sup>32</sup>:

$$\eta_{\rm int} = 5.2 \times 10^{-5} M_w^{0.76} \quad (\text{for } M_w \ge 35,000) \quad (14)$$

Figure 7 shows the plot of  $\ln[(_{\rm sp}/(\eta_{\rm int}C_{\rm polym})]$  as a function of  $\eta_{\rm int}C_{\rm polym}$  for the six isothermal cases. In this study, we used *model-predicted values* of  $x_m$  and  $M_w$  with the IOPs to generate values of  $\eta_{\rm int}C_{\rm polym}$ . It is observed from Figure 7 that no single value of  $K_M$  fits the entire range of experi-



**Figure 7** Plot of  $\ln[\eta_{sp}/(\eta_{int}C_{polym})]$  versus  $\eta_{int}C_{polym}$  for the isothermal data in Figure 3. Solid lines represent their best fits (second-order polynomials).

mental data. Dreval et al.<sup>33</sup> and Zakin et al.<sup>34</sup> reported similar plots for nonreacting polymer systems and observed that values of  $K_M$  are different for different ranges of  $\eta_{int}C_{polym}$ . Thus,  $K_M$  in the Martin equation can be treated as a curve-fit parameter. Our experimental data could be described by three straight lines having different slopes and intercepts.<sup>17</sup> However, for on-line optimizing control purposes, it would be better to have a continuous function applicable for the entire range of the abscissa in Figure 7 for any isothermal run. The form of eq. (9) can, thus, be modified (empirically) for the purpose of on-line optimizing control. We used the following function:

$$\ln \frac{\eta_{\rm sp}}{\eta_{\rm int} C_{\rm polym}} = d_0 + d_1 (\eta_{\rm int} C_{\rm polym}) + d_2 (\eta_{\rm int} C_{\rm polym})^2$$
(15)

In eq. (15),  $d_0$ ,  $d_1$ , and  $d_2$ , the constants, are determined by curve-fitting the experimental data on viscosity under isothermal conditions, using a least-squares fit. Table III gives these values along with the range of values of  $\eta_{\rm int}C_{\rm polym}$  over which they apply. The corresponding best-fit curves are shown in Figure 7 along with the experimental data. The fit is observed to be quite good.

Equation (15) can be rewritten using the definition of  $\eta_{\rm sp}$  as

$$\eta = \eta_{
m sol} [1 + \eta_{
m int} C_{
m polym} \exp\{d_0 + d_1(\eta_{
m int} C_{
m polym}) + d_2(\eta_{
m int} C_{
m polym})^2\}]$$
 (16)

Figure 8 shows model-predicted values of the viscosity of the reaction mixture using the IOP values (Table II) and values of  $d_0$ ,  $d_1$ , and  $d_2$  (Table

### Table III Best-fit Correlations<sup>25</sup> (BFCs)

 $\begin{array}{l} \log_{10} \left[ \theta_t(T), \, {\rm s} \right] = \, 124.1 \, - \, 1.0314 \, \times \, 10^5 \, (1/T) \, + \, 2.2735 \, \times \, 10^7 \, (1/T^2) \\ \log_{10} \left[ \theta_p(T), \, {\rm s} \right] = \, 80.3 \, - \, 7.50 \, \times \, 10^4 \, (1/T) \, + \, 1.765 \, \times \, 10^7 \, (1/T^2) \\ \log_{10} \left[ \theta_f(T), \, {\rm m^3 \ mol^{-1}} \right] = \, 198.6 \, - \, 1.455 \, \times \, 10^5 \, (1/T) \, + \, 2.70 \, \times \, 10^7 \, (1/T^2) \\ \end{array}$ 



**Figure 8** Comparison of experimental and model-predicted values of viscosity for the six sets of data under isothermal conditions. Parity line also shown.

III) plotted against the experimental values for the six different isothermal runs. The match around the parity line indicates that the correlation is satisfactory (correlation coefficient = 0.9769).

Figure 9 shows a comparison of the experimental viscosity data obtained for the two optimal temperature histories (Fig. 2) with model predictions. The inset shows the same data on magnified scales in the range of applicability of our viscosity correlations. To obtain model-predicted values of the viscosity corresponding to the actual temperature histories, the actual temperature history was first curve-fitted using a 17th-order Chebyshev series (code E02ADF from the NAG FORTRAN library). These coefficients were used in a simulation program to obtain model-predicted values of  $x_m$  and  $M_w$  using the best-fit correlations presented in Table IV. These were used for nonisothermal cases in several of our earlier studies<sup>4,18,19,22</sup> as well. The values of  $d_0$ ,  $d_1$ , and  $d_2$  at any temperature, used to generate the theoretical values of  $\eta(t)$ , are linearly interpolated values over corresponding ranges of temperature. It can be seen from Figure 9 that the agreement between the predicted and experimental values is excellent. In fact, we expect that a similar good agreement would be observed for *any* temperature history, not necessarily optimal.

Figure 9 also gives an idea of the sensitivity of values of viscosity to variations in the temperature history. The sharp increase in  $\eta(t)$  for the set-point and experimental temperature histories shown in Figure 2 were found to be displaced by a maximum of about 1 min. This much error is considered to be very reasonable, considering the dependence of  $\eta$  to the 3.4th power of  $M_w$  and (about) the fifth power of polymer concentration. In fact, the values of  $x_m$  and  $M_w$  for the two temperature histories are almost indistinguishable. It must be emphasized that no curve-fitting was done in generating Figure 9, and the excellent agreement between the model-predicted and experimental values of the viscosity suggests that we can, with confidence, use experimental data on  $\eta(t)$  and T(t) for state estimation purposes for on-line optimizing control of bulk polymerizations of systems exhibiting the Trommsdorff effect.

The existing PI controller on the Julabo circulator bath was sufficient to track the desired optimal temperature history reasonably closely in the present case, as seen in Figure 2. It was,



**Figure 9** Experimental data on viscosity for  $T_{opt}(t)$ . Curves show model predictions using set-point and experimental optimal temperature history (Fig. 2).

therefore, not necessary to reoptimize the temperature history on-line as the experimental T(t)never deviated significantly from the optimal history. However, with equipment failure such as failure of the circulating pump (at, say,  $t = t_1$ ) for any significant length of time, it will be necessary to find a new optimal history T(t) for  $t > t_1$ , online, for the remainder of the polymerization in order to reach the desired end product. This reoptimization will require the estimation of the state of the system at the time of equipment failure and reaction parameters (namely,  $\theta_t$ ,  $\theta_p$ , and  $\theta_f$ ) which will be estimated from the measured values of  $\eta(t)$  and T(t), for  $0 \le t \le t_1$ .

#### **CONCLUSIONS**

A model for predicting the viscosities of the reaction mass for any temperature history has been developed. It was demonstrated using a viscometer-reactor assembly developed in this work that the measured values of  $\eta(t)$  and T(t) along with a model can be used as a software sensor to estimate the state of the system and so help to monitor and control polymerization reactors on-line. The successful tracking of optimal temperature histories obtained off-line (using GA) was also shown. The computed viscosities for these nonisothermal temperature histories using the model

<i>T</i> (°C)	$I_0 \;({\rm mol/m^3})$	Range of Applicability	$d_{0}$	$d_1$	$d_2$
50	15.48	$26 \le \eta_{\rm int} C_{\rm polym} \le 95$	-5.75537	0.375202	-0.00179772
60	15.48	$21 \leq \eta_{\rm int} C_{\rm polym} \leq 85$	-4.33241	0.374597	-0.00192063
70	15.48	$21 \leq \eta_{\rm int} C_{\rm polym} \leq 35$	9.65985	-0.735517	0.0242187
50	25.80	$30 \le \eta_{\rm int} C_{\rm polym} \le 90$	-8.28148	0.475566	-0.00265283
60	25.80	$16 \leq \eta_{\rm int} C_{\rm polym} \leq 61$	-2.78061	0.372423	-0.00192133
70	25.80	$16 \le \eta_{ m int} C_{ m polym} \le 27$	26.4747	-2.48337	0.0736937

Table IV Values of  $d_0$ ,  $d_1$ , and  $d_2$  in Eqs. (15) and (16)

matched well with the measured values. Using the results from this work and following the theoretical work of Bhargava Ram et al.<sup>18</sup> and Garg et al.,<sup>19</sup> on-line optimizing control can now be easily implemented in our viscometer-reactor assembly. This work is now in progress and will be reported in a future communication. The knowledge gained on this system can easily be used for other free-radical homo- and copolymerizations which exhibit the gel, glass, and cage effects.

## NOMENCLATURE

$C_{\rm polvm}$	concentration of polymer (kg m <sup>-3</sup> )
$D_n^{r+1}$	dead polymer molecule having n re-
	peat units
$d_0 - d_2$	coefficients in viscosity equation
f	initiator efficiency at time $t$
$f_0$	initiator efficiency in the limiting
	case of zero diffusional resistance
Ι	initiator
$I_0$	concentration of initiator at $t = 0$
	$(\text{mol } \text{m}^{-3})$
IOP	individually optimized values of pa-
	rameters
$K_M$	empirical parameter in Martin's
	equation
$k_d, k_p, k_t$	rate constants for initiation, propa-
	gation, and termination in the
	presence of the gel and glass effects
	$(s^{-1}, \text{ or } m^3 \text{ mol}^{-1} s^{-1})$
$k_{tc}, k_{td}$	rate constants for termination by
	combination or by disproportion-
	ation in the presence of the gel ef-
	fect $(m^3 mol^{-1} s^{-1})$
$k_{td,0}, k_{p,0}$	$k_{td}$ and $k_p$ in absence of gel or glass
	effects $(m^3 mol^{-1} s^{-1})$
M	monomer; moles of monomer in the
	liquid phase (mol)
$M_w$	weight-average molecular weight
	$\begin{bmatrix} \equiv (MW_m)(\lambda_2 + \mu_2)/(\lambda_1 + \mu_1) \end{bmatrix}$
-	$(\text{kg mol}^{-1})$
$P_n$	growing polymer radical having <i>n</i> re-
	peat units
р	vector representing the model pa-
D	rameters, $\theta_t$ , $\theta_p$ , $\theta_f$
R	primary radical
S T(1)	moles of solvent in liquid phase (mol)
T(t)	temperature of the reaction mixture $(K = 20)$
,	at time $t$ (K or $C$ )
ι	unie (min)
u v v	control vector (scalar, $u$ , in this work)
$u_{\min}, u_{\max}$	lower and upper bounds on the con-
	uroi variable

$V_l$	volume of liquid at time $t$ (m <sup>3</sup> )
$w_1, w_2$	weighting factors
x	vector representing state variables
$x_m(t)$	monomer conversion (molar) at time
	$t \equiv 1 - 1 (M/(\zeta_{m1}))$

#### **Greek Letters**

$egin{aligned} & \gamma \ & \zeta_m, \ & \zeta_{m1} \ & \eta \ & \eta_{ ext{int}} \ & \eta_{ ext{sol}} \ & \eta_{ ext{sol}} \ & \eta_{ ext{sp}} \ &  heta_t, \ &  heta_p, \ &  heta_f \ & \lambda_k \end{aligned}$	shear rate at time $t$ (s <sup>-1</sup> ) net monomer added to the reactor as defined by Seth and Gupta <sup>25</sup> viscosity of the reaction mass (Pa s) intrinsic viscosity (m <sup>3</sup> kg <sup>-1</sup> ) solvent (monomer) viscosity (Pa s) specific viscosity (dimensionless) adjustable parameters in the model (s, s, and m <sup>3</sup> mol <sup>-1</sup> ) $k$ th ( $k = 0, 1, 2 \dots$ ) moment of live
$\mu_k$	$(P_n) \text{ polymer radicals} \equiv \sum_{n=1}^{\infty} n^k P_n]$ (mol) $k \text{th } (k=0, 1, 2 \dots) \text{ moment of dead}$ $(D_n) \text{ polymer chains} \equiv \sum_{n=1}^{\infty} n^k D_n]$
$\mu_n$ $\xi_{I3}, \xi_{I3}$ $ ho_m,  ho_p$	(mol) number-average chain length at time $t \ [\equiv (\lambda_1 + \mu_1)/(\lambda_0 + \mu_0)]$ ratio of the molar volume of the monomer and initiator jumping units to the critical molar volume of the polymer, respectively density of pure (liquid) monomer and polymer at temperature <i>T</i> (kg
$egin{array}{ll}  au \ \phi_m, \ \phi_p \ \psi, \ \psi_{ m ref} \end{array}$	$m^{-3}$ ) shear stress (Pa) volume fractions of monomer and polymer in liquid at time t free-volume parameters [see Bhar- gava Ram et al. <sup>18</sup> ]

#### Subscripts/Superscripts

d	desired value
f	final value
0	initial value
opt	optimal value

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