

Sensitivity Analysis of a Batch Polymerization Reactor

ISABELLE M. THOMAS and COSTAS KIPARISSIDES, *Department of Chemical Engineering, University of Alberta, Edmonton, Alberta T6G 2G6, Canada*

Synopsis

The sensitivity of model output variables for a batch polymerization reactor to uncertainties in the kinetic parameters and initial conditions is studied. Differential equations that describe the time variation of sensitivity coefficients for the batch reactor are derived. Numerical integration of the sensitivity equations reveals that the system output responses are very sensitive to parameter variations especially when the polymerization exhibits an autoacceleration of the reaction rate.

INTRODUCTION

There have been a large number of experimental and theoretical investigations published on batch and continuous free radical polymerization reactors. Of the reported papers, many studies are concerned with the modeling and optimization of polymerization reactors. However, in spite of all this modeling activity, little has been published on the sensitivity analysis of these models. Sensitivity analysis is concerned with the deviations of model output responses caused by deviation of system parameters from their nominal values. Polymerization reactors are usually modeled in terms of a set of nonlinear ordinary differential equations which possess a number of parameters, including rate constants, initial conditions, reactor temperature, and transport coefficients. Since it is not possible for us to know precisely the numerical values of model parameters, it is necessary to look into the sensitivity problem and determine how the parameter uncertainties affect the output variables of the system.

The present work is concerned with the sensitivity analysis of a batch free radical polymerization reactor for methyl methacrylate (MMA). Four nonlinear ordinary differential equations in terms of initiator concentration, monomer conversion, zero moment, and second moment of the MWD are used to describe the dynamics of the batch system. To account for the conversion dependence of the termination and propagation rate constants, a gel effect function is introduced. Based on this model the differential equations governing the time variation of the sensitivity matrix are derived.

REACTOR MODEL

Free radical polymerization reactors can be modeled in terms of a set of nonlinear differential equations. Derivation of these equations will not be attempted here for many modeling studies on this subject have been reported in the liter-

* Dr. C. Kiparissides is presently with the Department of Chemical Engineering, University of Thessaloniki, Thessaloniki, Greece.

ature.¹⁻³ The modeling equations that describe the time variation of initiator concentration, monomer conversion, and zero and second moment of molecular weight distribution (MWD), in a batch reactor for the polymerization of methylmethacrylate (MMA), are written as⁴

$$\frac{dI}{dt} = -k_d I \quad (1)$$

$$\frac{dX}{dt} = (2fk_d I)^{1/2} \frac{k_p}{k_{td}^{1/2}} (1 - X) \quad (2)$$

$$\frac{d\mu_0}{dt} = 2fk_d I \quad (3)$$

$$\frac{d\mu_2}{dt} = 2 \frac{k_p^2}{k_{td}} M_0^2 (1 - X)^2 \quad (4)$$

where I is the initiator concentration, X the monomer conversion, and μ_0 and μ_2 are the zero and second moment of MWD, respectively. The parameters which appear in the modeling eqs. (1)–(4), are the initiator efficiency f , the initiator decomposition rate constant k_d , and the ratio of the square of the propagation rate constant k_p over the termination rate constant, k_{td} , ($K_2 = k_p^2/k_{td}$). Experimental data⁵⁻⁷ have shown that the termination and propagation rate constants vary with the time due to the gel effect or Trommsdorf effect. As a result of this, the parameter K_2 can be expressed as

$$K_2 = K_{20} \cdot g(X, T) \quad (5)$$

where K_{20} is the value of K_2 at $X = 0$ and $g(X, T)$ is the gel effect function that accounts for the conversion and temperature dependence of k_p and k_{td} .

Due to the gel effect the termination rate constant decreases, which results in an increase of the polymerization rate in the conversion range of 20–80%. Beyond this range, even the propagation reaction becomes diffusion controlled, which causes a dramatic decrease in the polymerization rate. To account for this type of behavior of K_2 , an exponential relationship of $g(X, T)$ on X and T was assumed. Friis and Hamielec⁶ had earlier proposed a similar expression

$$g(X, T) = \exp(AX^3 + BX^2 + CX) \quad (6)$$

with

$$A = A_1/T + A_2, \quad B = B_1/T + B_2, \quad C = C_1/T + C_2 \quad (7)$$

The parameters A_1, A_2, \dots, C_2 were estimated by fitting the model eqs. (1)–(7) to the experimental data of Balke.⁸ A Levenberg–Marquardt routine for solving nonlinear least squares problems was used to estimate the unknown parameters. Because of the high sensitivity of the system responses to the parameters of the gel effect function, extra care had to be taken in selecting the initial values of these parameters. Numerical values of the kinetic parameters of the model and estimates of the parameters A_1, A_2, \dots, C_2 are given in Appendix A.

SENSITIVITY ANALYSIS

Although the mathematical model developed in this work describes satisfactorily the polymerization of methyl methacrylate in a batch reactor, yet our knowledge of the kinetic parameters may be imperfect. This gives rise to the important problem of parameter sensitivity. The aim of this analysis is to find the effects of parameter uncertainties on the calculated output responses. In our case we study the effects of parameter uncertainties in k_d , f , K_2 , on the calculated values of $[I]$, X , μ_0 , μ_2 . In addition to the sensitivity of the system responses to the above parameters, we are also interested in knowing the effects of the initial initiator concentration $[I_0]$ and polymerization temperature T on the output variables.

As we saw earlier, the polymerization of MMA in a batch reactor can be described by a set of four differential eqs. (1)–(4), which can be written in a vector form as

$$\dot{\mathbf{Z}} = \mathbf{f}(\mathbf{Z}, \mathbf{p}, t), \quad \mathbf{Z}(t_0) = \mathbf{Z}_0, \quad (8)$$

where \mathbf{Z} is the output vector and \mathbf{p} the parameter vector, defined by

$$\mathbf{Z} = (I, X, \mu_0, \mu_2)^T \quad (9)$$

$$\mathbf{p} = (k_d, f, K_2, A_1, A_2, B_1, B_2, C_1, C_2, T, I_0)^T \quad (10)$$

The sensitivity coefficient for the parameter p_j and the output Z_i is defined as the first partial derivative of Z_i with respect to p_j

$$\Phi_{ij} = \frac{\partial Z_i}{\partial p_j}, \quad i = 1, \dots, 4, \quad j = 1, \dots, 11 \quad (11)$$

Sensitivity coefficients indicate the magnitude and the direction of change of the response Z due to perturbations in the values of the parameters. For a vector of output variables \mathbf{Z} the matrix of the derivatives with respect to the parameters \mathbf{p} is called the sensitivity matrix (Φ_{ij}) :

$$(\Phi_{ij}) = \left(\frac{\partial Z_i}{\partial p_j} \right) = \left(\frac{\partial \mathbf{Z}}{\partial \mathbf{p}} \right) \quad (12)$$

The information provided by the model must be used to determine $(\partial \mathbf{Z} / \partial \mathbf{p})$. However, since eqs. (8) cannot be integrated analytically, the sensitivity matrix cannot be calculated analytically from eq. (12). Following the analysis of Atherton et al.⁹ and Beck and Arnold,¹⁰ a differential equation for the sensitivity matrix is derived. This is obtained by interchanging the order of differentiation in the expression below and using eq. (8)

$$\frac{d}{dt} \left(\frac{\partial \mathbf{Z}}{\partial \mathbf{p}} \right) = \frac{\partial}{\partial \mathbf{p}} \left(\frac{d \mathbf{Z}}{dt} \right) = \frac{\partial f(\mathbf{Z}, \mathbf{p}, t)}{\partial \mathbf{p}} \quad (13)$$

Since \mathbf{Z} is a function of \mathbf{p} , the right-hand expression is expanded to give

$$\frac{d}{dt} \left(\frac{\partial \mathbf{Z}}{\partial \mathbf{p}} \right) = \left(\frac{\partial f}{\partial \mathbf{Z}} \right) \Big|_{\mathbf{p}} \left(\frac{\partial \mathbf{Z}}{\partial \mathbf{p}} \right) + \left(\frac{\partial f}{\partial \mathbf{p}} \right) \Big|_{\mathbf{Z}} \quad (14)$$

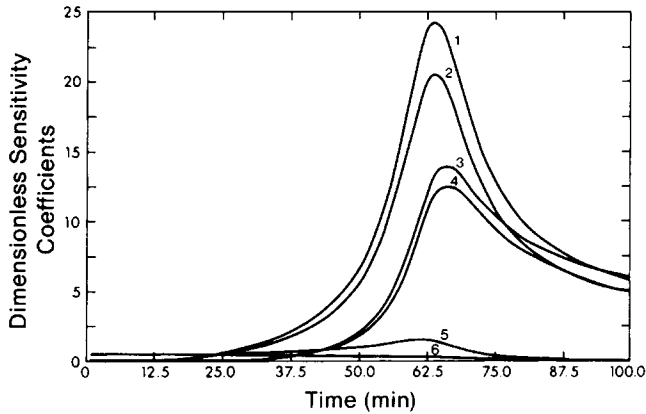


Fig. 1. The effect of parameter perturbations on the conversion ($I_0 = 0.017 \text{ mol} \cdot \text{L}^{-1}$, $T = 70^\circ\text{C}$): (1) B_1 ; (2) B_2 ; (3) A_1 ; (4) A_2 ; (5) K_{20} ; (6) k_d, f, C_1, C_2 .

Introducing the sensitivity coefficients, Φ_{ij} , eq. (14) is written as

$$\frac{d\Phi_{ij}}{dt} = \sum_l \frac{\partial f_i}{\partial Z_l} \Phi_{lj} + \frac{\partial f_i}{\partial p_j} \quad i, l = 1, \dots, 4, \quad j = 1, \dots, 11 \quad (15)$$

The initial conditions for eq. (15) are summarized as

$$\Phi_{ij}(0) = \begin{cases} 0 & \text{if } p_j \text{ is not an initial condition} \\ \delta_{ij} & \text{if } p_j \text{ is an initial condition} \end{cases} \quad (16)$$

From the numerical integration of the differential eq. (15) with the initial conditions (16), we obtain the complete time history of the sensitivity coefficients. The total number of the sensitivity equations is equal to the number of state variables times the number of parameters (i.e., 4×11). The differential equations that describe the time variation of the sensitivity coefficients for the batch reactor are derived in Appendix B.

The results of the integration of the sensitivity equations for k_d, f, K_{20}, A_1 ,

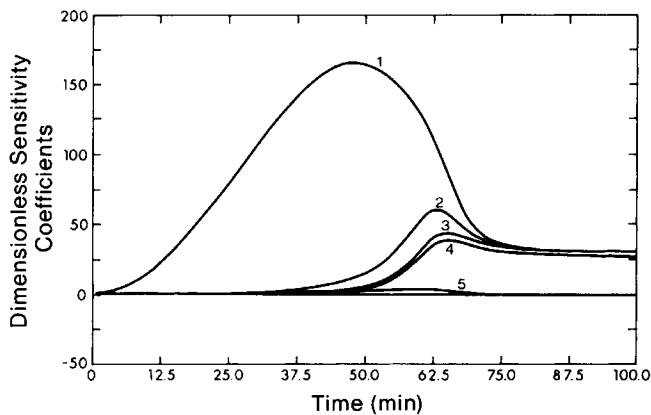


Fig. 2. The effect of parameter perturbations on the second moment of MWD ($I_0 = 0.017 \text{ mol} \cdot \text{L}^{-1}$, $T = 70^\circ\text{C}$): (1) B_1 ; (2) B_2 ; (3) A_1 ; (4) A_2 ; (5) k_d, f, k_{20}, C_1, C_2 .

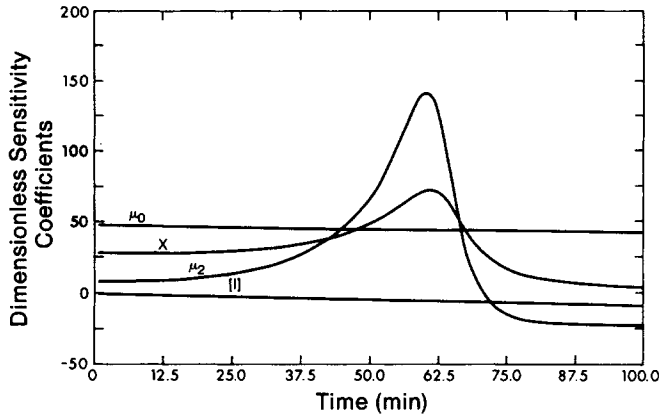


Fig. 3. The effect of temperature perturbations on the system responses ($I_0 = 0.017 \text{ mol} \cdot \text{L}^{-1}$).

B_1, C_1, A_2, B_2, C_2 are summarized in Figures 1 and 2. In order to show the relative influence of the parameters on the output variables, normalized sensitivity coefficients defined by eq. (17) are plotted:

$$\rho_{ij} = \Phi_{ij}(p_j/Z_i) \tag{17}$$

A positive sensitive coefficient indicates that a positive variation of the corresponding parameter causes an increase in the output variable. A negative sensitivity coefficient indicates that a positive variation of the parameter results in a decrease in the output variable. It is seen that the output variables are most sensitive to A_1, B_1, A_2, B_2 parameters, Figures 1 and 2.

An increase in k_d or in f does not cause any significant perturbation on the initiator concentration and the zero moment; however, it causes a slight increase in monomer conversion and a slight decrease in second moment at the end of the reaction (Figs. 1 and 2).

The effect of temperature perturbations on the system outputs is shown in Figure 3. An increase in temperature results in an increase in monomer con-

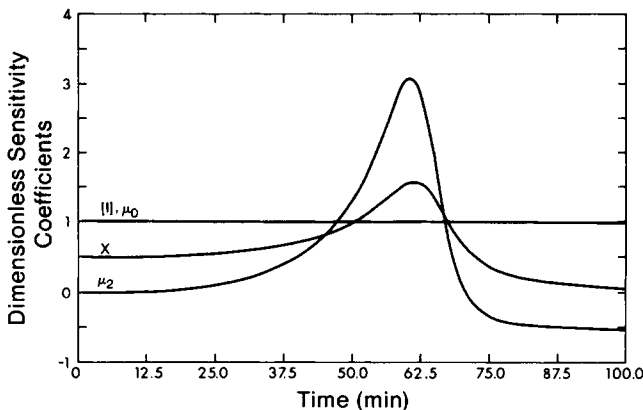


Fig. 4. The effect of perturbations in the initial initiator concentration on the system responses ($T = 70^\circ\text{C}$).

version and zero moment, a small decrease in initiator concentration, and a decrease in second moment at the end of reaction.

The effect of perturbations in the initial concentration of catalyst $[I_0]$ on the system responses is shown in Figure 4. The output variables are much less sensitive to $[I_0]$ than to T . However, the profiles of the corresponding sensitivity coefficients have similar shapes. An increase in $[I_0]$ causes an increase in monomer conversion and zero moment and a decrease in the second moment at the end of the reaction.

The quantitative interpretation of Figures 1–4 shows how accurate the estimates of the kinetic parameters should be. As an example, consider the effect of a perturbation in B_1 on the conversion X . From Figure 1, it can be seen that the dimensionless sensitivity coefficient ρ_{26} can take values up to 25. For a value of ρ_{26} equal to 25, eq. (17) becomes

$$\rho_{26} = 25 = \frac{B_1}{X} \cdot \frac{\partial X}{\partial B_1} \quad (18)$$

For a small perturbation in B_1 (i.e., 1%), $\partial X/\partial B_1$ can be approximated by $\Delta X/\Delta B_1$. Therefore,

$$\frac{\Delta X}{X} = \frac{\Delta B_1}{B_1} \cdot \rho_{26} = \frac{1}{100} \cdot 25 = 25\%$$

This means that a 1% perturbation in B_1 (B_1 changes from 75,000 to 75,750) could result in a 25% variation in monomer conversion.

CONCLUSIONS

The application of the sensitivity analysis to the system equations has revealed that the system output responses are very sensitive to parameter variations especially when the polymerization exhibits an autoacceleration of the rate of reaction. We have shown quantitatively that in the conversion range where the rate constants become diffusion controlled the system responses can vary from 0–150% as a result of small perturbations in the kinetic parameters. In particular, it has been shown that the second moment of the MWD and the monomer conversion are very sensitive to the polymerization temperature and kinetic parameters A_1, A_2, B_1, B_2 of the gel effect function.

The results of this paper on the sensitivity analysis have provided valuable information for the study of optimal control of polymerization reactors.⁴ In particular, Figures 3 and 4 show that an increase in temperature or initiator concentration will have initially a positive effect on both monomer conversion and second moment of the MWD (positive sensitivity coefficients), while at the end of the polymerization a similar change will cause an increase in the monomer conversion and a decrease in the second moment. This means that, after a certain conversion, the system variables, conversion, and second moment of the MWD will react in opposite directions to manipulations of the control variables (initiator concentration, temperature), thus making the simultaneous control of these variables impossible. It should be noted that the sensitivity coefficients for μ_0 and I do not remain constant with time (Figs. 3 and 4). In fact, they vary slightly with time. The observed small variation in these coefficients is due to the almost constant initiator concentration during polymerization.

Finally we must point out that the sensitivity coefficients can provide insight into the cases for which parameters can and cannot be estimated. Actually, parameters in an algebraic or differential equation can be uniquely estimated if the sensitivity coefficients are not linearly dependent over the range of experimental measurements.

APPENDIX A

Numerical Values of the Kinetic Parameters

$$\begin{aligned} f &= 0.6 \\ k_d &= 1.35 \times 10^{-6} \exp(-16298.0/T) \quad (\text{s}^{-1}) \\ K_{20} &= 100.4 \exp(-2960.0/T) \quad (\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}) \\ [I_0] &= 0.017 \quad (\text{mol}\cdot\text{L}^{-1}) \\ M_0 &= 9.3 \quad (\text{mol}\cdot\text{L}^{-1}) \end{aligned}$$

Estimates of the Parameters in $g(X,T)$

$$\begin{aligned} A_1 &= -9.65 \times 10^4 \text{ (K)}, & A_2 &= 2.50 \times 10^2 \\ B_1 &= 7.50 \times 10^4 \text{ (K)}, & B_2 &= 1.85 \times 10^2 \\ C_1 &= -2.50 \times 10 \text{ (K)}, & C_2 &= -2.50 \times 10^{-1} \end{aligned}$$

APPENDIX B: DERIVATION OF THE SENSITIVITY EQUATIONS

The bulk polymerization of MMA in a batch reactor is described by the following set of differential equations:

$$\begin{aligned} \dot{Z}_1 &= -k_d Z_1 + F_c/V \\ \dot{Z}_2 &= (2fk_d Z_1 K_2)^{1/2} \cdot (1 - Z_2) \\ \dot{Z}_3 &= 2fk_d Z_1 \\ \dot{Z}_4 &= 2K_2 M_0^2 (1 - Z_2)^2 \end{aligned} \tag{19}$$

where the overdot denotes the time derivative of a variable (d/dt) (). Z is the output vector

$$Z = (Z_1, Z_2, Z_3, Z_4)^T = (I, X, \mu_0, \mu_2)^T$$

and

$$K_2 = K_{20} \cdot \exp(AZ_2^2 + BZ_2 + C) = K_{20} \cdot g(Z_2, T)$$

Application of sensitivity eqs. (15) and (16) to the system of eq. (19) yields the following differential equations for the sensitivity coefficients:

For the dissociation rate constant k_d :

$$\begin{aligned} \dot{\Phi}_{11} &= S_1 \Phi_{11} - Z_1 \\ \dot{\Phi}_{21} &= S_2 \Phi_{11} + S_3 \Phi_{21} + (fK_2 Z_1 / 2k_d)^{1/2} (1 - Z_2) \\ \dot{\Phi}_{31} &= S_4 \Phi_{11} + 2fZ_1 \\ \dot{\Phi}_{41} &= S_5 \Phi_{21} \end{aligned} \tag{20}$$

I.C. $\Phi_{i1}(0) = 0, \quad i = 1, \dots, 4$

where S_1, S_2, S_3, S_4, S_5 are defined as

$$\begin{aligned} S_1 &= -k_d, & S_2 &= (fk_d K_2 / 2Z_1)^{1/2} (1 - Z_2) \\ S_3 &= [1/2(3AZ_2^2 + 2BZ_2)(1 - Z_2) - 1](2fk_d Z_1 K_2)^{1/2} \\ S_4 &= 2fk_d \\ S_5 &= [-2 + (1 - Z_2)(3AZ_2^2 + 2BZ_2)][2K_2 M_0^2 (1 - Z_2)] \end{aligned}$$

For the initiator efficiency f :

$$\begin{aligned}\dot{\Phi}_{12} &= S_1\Phi_{12} \\ \dot{\Phi}_{22} &= S_2\Phi_{12} + S_3\dot{\Phi}_{22} + (k_dK_2Z_1/2f)^{1/2}(1 - Z_2) \\ \dot{\Phi}_{32} &= S_4\Phi_{12} + 2k_dZ_1 \\ \dot{\Phi}_{42} &= S_5\dot{\Phi}_{22}\end{aligned}\quad (21)$$

I.C. $\Phi_{i2}(0) = 0, \quad i = 1, \dots, 4$

For K_{20} ($K_{20} = k_p^2/k_t$ at $X = 0$):

$$\begin{aligned}\dot{\Phi}_{13} &= S_1\dot{\Phi}_{13} \\ \dot{\Phi}_{23} &= S_2\dot{\Phi}_{13} + S_3\dot{\Phi}_{23} + (k_d f Z_1 g / 2K_{20})^{1/2}(1 - Z_2) \\ \dot{\Phi}_{33} &= S_4\dot{\Phi}_{13} \\ \dot{\Phi}_{43} &= S_5\dot{\Phi}_{23} + 2 \exp(AZ_2^3 + BZ_2^2 + C) \cdot M_0^2(1 - Z_2)^2\end{aligned}\quad (22)$$

I.C. $\Phi_{i3}(0) = 0, \quad i = 1, \dots, 4$

For parameter A_1 :

$$\begin{aligned}\dot{\Phi}_{14} &= S_1\dot{\Phi}_{14} \\ \dot{\Phi}_{24} &= S_2\dot{\Phi}_{14} + S_3\dot{\Phi}_{24} + (Z_2^3/2T)(2fk_dZ_1K_2)^{1/2}(1 - Z_2) \\ \dot{\Phi}_{34} &= S_4\dot{\Phi}_{14} \\ \dot{\Phi}_{44} &= S_5\dot{\Phi}_{24} + 2(Z_2^3/T)K_2M_0^2(1 - Z_2)^2\end{aligned}\quad (23)$$

I.C. $\Phi_{i4}(0) = 0, \quad i = 1, \dots, 4$

For parameter A_2 :

$$\begin{aligned}\dot{\Phi}_{15} &= S_1\dot{\Phi}_{15} \\ \dot{\Phi}_{25} &= S_2\dot{\Phi}_{15} + S_3\dot{\Phi}_{25} + (Z_2^3/2)(2fk_dZ_1K_2)^{1/2}(1 - Z_2) \\ \dot{\Phi}_{35} &= S_4\dot{\Phi}_{15} \\ \dot{\Phi}_{45} &= S_5\dot{\Phi}_{25} + 2Z_2^3K_2M_0^2(1 - Z_2)^2\end{aligned}\quad (24)$$

I.C. $\Phi_{i5}(0) = 0, \quad i = 1, \dots, 4$

For parameter B_1 :

$$\begin{aligned}\dot{\Phi}_{16} &= S_1\dot{\Phi}_{16} \\ \dot{\Phi}_{26} &= S_2\dot{\Phi}_{16} + S_3\dot{\Phi}_{26} + Z_2^2/2T(2fk_dZ_1K_2)^{1/2}(1 - Z_2) \\ \dot{\Phi}_{36} &= S_4\dot{\Phi}_{16} \\ \dot{\Phi}_{46} &= S_5\dot{\Phi}_{26} + 2(Z_2^2/T)M_0^2K_2(1 - Z_2)^2\end{aligned}\quad (25)$$

I.C. $\Phi_{i6}(0) = 0, \quad i = 1, \dots, 4$

For parameter B_2 :

$$\begin{aligned}\dot{\Phi}_{17} &= S_1\dot{\Phi}_{17} \\ \dot{\Phi}_{27} &= S_2\dot{\Phi}_{17} + S_3\dot{\Phi}_{27} + (Z_2^3/2)(2fk_dZ_1K_2)^{1/2}(1 - Z_2) \\ \dot{\Phi}_{37} &= S_4\dot{\Phi}_{17} \\ \dot{\Phi}_{47} &= S_5\dot{\Phi}_{27} + 2Z_2^3K_2M_0^2(1 - Z_2)^2\end{aligned}\quad (26)$$

I.C. $\Phi_{i7}(0) = 0, \quad i = 1, \dots, 4$

For parameter C_1 :

$$\begin{aligned}\dot{\Phi}_{18} &= S_1\dot{\Phi}_{18} \\ \dot{\Phi}_{28} &= S_2\dot{\Phi}_{18} + S_3\dot{\Phi}_{28} + (1/2T)(2fk_dZ_1K_2)^{1/2}(1 - Z_2) \\ \dot{\Phi}_{38} &= S_4\dot{\Phi}_{18} \\ \dot{\Phi}_{48} &= S_5\dot{\Phi}_{28} + (2/T)K_2M_0^2(1 - Z_2)^2\end{aligned}\quad (27)$$

I.C. $\Phi_{i8}(0) = 0, \quad i = 1, \dots, 4$

For parameter C_2 :

$$\begin{aligned} \Phi_{19} &= S_1 \Phi_{19} \\ \dot{\Phi}_{29} &= S_2 \Phi_{19} + S_3 \Phi_{29} + \frac{1}{2}(2fk_d Z_1 K_2)^{1/2}(1 - Z_2) \\ \dot{\Phi}_{39} &= S_4 \Phi_{19} \\ \dot{\Phi}_{49} &= S_5 \Phi_{29} + 2K_2 M_0^2 (1 - Z_2)^2 \end{aligned} \quad (28)$$

I.C. $\Phi_{i9}(0) = 0, \quad i = 1, \dots, 4$

For temperature T :

$$\begin{aligned} \Phi_{110} &= S_1 \Phi_{110} - (E_d/T^2)k_d Z_1 \\ \dot{\Phi}_{210} &= S_2 \Phi_{110} + S_3 \Phi_{210} + (1/2T^2) \\ &\quad \times (+E_d + E_2 - A_1 Z_2^3 - B_1 Z_2^2 - C_1)(2fk_d Z_1 K_2)^{1/2}(1 - Z_2) \\ \dot{\Phi}_{310} &= S_4 \Phi_{110} + 2(E_d/T^2)fk_d Z_1 \\ \dot{\Phi}_{410} &= S_5 \Phi_{210} + (2/T^2)[E_2 - A_1 Z_2^3 - B_1 Z_2^2 - C_1]K_2 M_0^2 (1 - Z_2)^2 \end{aligned} \quad (29)$$

I.C. $\Phi_{i10}(0) = 0, \quad i = 1, \dots, 4$

For initial initiator concentration $[I_0]$

$$\begin{aligned} \Phi_{111} &= S_1 \Phi_{111} \\ \dot{\Phi}_{211} &= S_2 \Phi_{111} + S_3 \Phi_{211} \\ \dot{\Phi}_{311} &= S_4 \Phi_{111} \\ \dot{\Phi}_{411} &= S_5 \Phi_{211} \end{aligned} \quad (30)$$

I.C. $\Phi_{111}(0) = 1, \quad \Phi_{i11}(0) = 0, \quad i = 2, \dots, 4$

The numerical integration of the sensitivity equations has been performed along with the numerical integration of the state equations, using a fourth order Runge–Kunta routine with variable step size. It should be noted that the sensitivity equations are very stiff and extra care must be taken in integrating these equations.⁹ Another method of solution is to represent $(\partial Z_i / \partial p_j)$ as a finite difference and compute values of the state variables for small perturbations in the parameters p :

$$\frac{\partial Z_i}{\partial p_j} = \Phi_{ij} = \frac{Z_i(p_1, \dots, p_j + \delta p_j, \dots) - Z_i(p_1, \dots, p_j, \dots)}{\delta p_j}$$

Following the recommendation of Beck and Arnold,¹⁰ δp_j has been chosen equal to $\delta p_j = 0.0001 P_j$. This simple procedure is often quite satisfactory. In this work, sensitivity coefficients calculated by the two methods did not vary significantly.

APPENDIX C: NOMENCLATURE

f	initiator efficiency
$g(X, T)$	gel effect function, $g(X, T) = K_2/K_{20}$
I	initiator concentration ($\text{gmol} \cdot \text{L}^{-1}$)
I_0	initiator concentration at time $t = 0$ ($\text{gmol} \cdot \text{L}^{-1}$)
k_d	rate constant for dissociation of initiator (s^{-1})
k_p	propagation rate constant ($\text{L} \cdot \text{gmol}^{-1} \cdot \text{s}^{-1}$)
k_{td}	rate constant for termination by disproportionation ($\text{L} \cdot \text{gmol}^{-1} \cdot \text{s}^{-1}$)
K_2	$K_2 = k_p^2/k_{td}$ ($\text{L} \cdot \text{gmol}^{-1} \cdot \text{s}^{-1}$)
K_{20}	K_2 at conversion $X = 0$ ($\text{L} \cdot \text{gmol}^{-1} \cdot \text{s}^{-1}$)
M	monomer concentration ($\text{gmol} \cdot \text{L}^{-1}$)
M_0	monomer concentration at time $t = 0$ ($\text{gmol} \cdot \text{L}^{-1}$)
\mathbf{p}	parameter vector
t	time
T	polymerization temperature ($^\circ\text{K}$)
X	monomer conversion
\mathbf{Z}	system output vector, $\mathbf{Z} = ([I], X, \mu_0, \mu_2)^T$

μ_k	k th moment of the dead polymer distribution ($\text{gmol} \cdot \text{L}^{-1}$)
ρ_{ij}	normalized sensitivity coefficient
Φ_{ij}	sensitivity coefficient

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