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PARAMETRIC SENSITIVITY OF FREE RADICAL POLYMERIZATION ASSOCIATED WITH GEL AND GLASS EFFECTS

C. PETRILA and S. CURTEANU

(Department of Chemical Engineering, Technical University "Gh. Asachi", IASI B-dul D. Mangeron 71A, 6600 IASI, ROMANIA)

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The parametric sensitivity is studied of an isothermal homopolymerization system exhibiting the gel and glass effects. As example, the initiated radical polymerization of methyl methacrylate to be achieved in a batch bulk process is considered. For the diffusion controlled reactions, a simple model was proposed containing the dependencies of termination and propagation rate constants with monomer conversion, initiator concentration and temperature. The easiness of handling it and the good agreement between simulation and experimental results are the main features of these models, recommending them for complex engineering studies. The sensitivities of the state variables (initiator concentration, monomer conversion and distribution moments of the chain length) and the model outputs (numerical and gravimetrical average polymerization degrees) with respect to various parameters are computed. It is found that the temperature has the strongest influence in the polymerization process, so it is necessary the stabilization of this parameter with a control loop. The analysis shows that the propagation and initiation activation energies are two of the most important parameters governing the system performance. Almost all the system parameters have the greatest influence at the gel effect moment. Using a calculus based on sensitivity functions, the quantitative estimation of the parameter influence on the system state and output variables are made.

Keywords: free radical polymerization, sensitivity analysis, metyl methacrylate

Introduction

Several constraints are faced in the design of chain polymerization reactors, particularly those exhibiting the gel effect: the large heat of reaction, the low thermal diffusivity and the high viscosity of the reaction mixture. Hence, in the design or operation of systems of this type it becomes important to know, *a priori*, the limits on values of the various parameters associated with the reaction system, arising because of these constraints. These are referred to as *parametric sensitivities boundaries* and represent conditions at which different state variables, like conversion or molecular weight become extremely sensitive to small changes in the input parameters. These sensitivity studies also help in identifying parameters which are most critical, and which must, therefore, be controlled or estimated precisely.

Considerable work has been reported on the parametric sensitivity of chemical systems, but less concerning polymerization processes because of the complexity of these systems and the difficulties involved by their models. Studies on parametric sensitivity of polymerization systems started with those of Biesenberger *et al.* [1]. These prior works on thermal runaway in chain polymerizations and copolymerizations were limited to systems which do not exhibit the gel effect. Baillagou and Soong [2, 3] realize a parametric sensitivity study for a system exhibiting the gel effect, but the study is somewhat restrictive because it follows an intuitive criteria. Tjahjadi *et al.* [4] have studied temperature and molecular weight sensitivities in plug-flow (or well-mixed batch) homopolymerization reactors in the absence of the gel effect. Their work is mathematically more precise and less intuitive in nature and uses as example the low density polyethylene system. Kapoor, Gupta and Varma [5] developed a mathematical technique for studying the parametric sensitivity of reactors including chain polymerization systems exhibiting the gel and glass effects. They used the model of Chiu *et al.* [6] for the gel and glass effects. This model considers diffusional effects as an integral part of termination and propagation reactions just from the beginning of the polymerization process. The sensitivities of the two temperature maxima with respect

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Contact information: E-mail: scurtean@ch.tuiasi.ro; Silvia Curteanu, Eternitate str., nr.69a, 6600 IASI, ROMANIA

to various parameters are computed. It is found that all the sensitivities of the gel effect induced temperature peak attain their maximum at the same conditions. This sensitivity boundary is associated with high conversions and high molecular weights.

The present work is a first part of a complex study starting with parametric sensitivity of the isothermal bulk free radical polymerization of methyl methacrylate in well-mixed batch reactors. It must be emphasized that new correlations for diffusion controlled reactions (gel and glass effects) were used. Also, a simple algorithm for sensitivity calculus was used, different of that of the above attempts. To provide practical constraints on reactor design and operation, the qualitative and quantitative estimations of the various parameters influences on the system state and output are made. The quantitative predictions related to polymerization process are very important.

Kinetic Model

The initiated radical polymerization of methyl methacrylate (MMA) is considered to be achieved in a batch bulk process. For this reaction, the following kinetic diagram is used:

Initiation

$$\begin{cases} I \xrightarrow{k_d} 2R^* \\ R^* + M \xrightarrow{k_i} P_1^* \end{cases}$$

Propagation

$$P_n^* + M \xrightarrow{k_p} P_{n+1}^*$$

Chain transfer to monomer

$$P_n^* + M \xrightarrow{k_{tm}} D_n + P_1^*$$

Termination by disproportionation

$$P_n^* + P_m^* \xrightarrow{k_t} D_n + D_m$$

where I, M and R^* represent the initiator, monomer, and primary radical, respectively; P_n^* and D_n are the macroradical and the dead polymer with n monomer units; k_d, k_i, k_p, k_{tm}, k_t are rate constants for initiator decomposition, initiation, propagation, chain transfer to monomer, and termination by disproportionation, respectively.

Based on the kinetic diagram, one can write the material balance equations for monomer conversion (x), concentration of the initiator (I), and moments of radicals (λ_k) and dead polymer (μ_k) (k = 0,1,2), which give the distribution of the chain length:

$$\frac{dI}{dt} = -k_d I - I\varepsilon \frac{1-x}{1+\varepsilon x} \lambda_0 (k_p + k_{tm}) \tag{1}$$

$$\frac{dx}{dt} = (k_p + k_{tm})(1-x)\lambda_0 \tag{2}$$

$$\frac{d\lambda_0}{dt} = 2fk_d I - k_t \lambda_0^2 - \lambda_0^2 \varepsilon \frac{1-x}{1+\varepsilon x}(k_p + k_{tm}) \tag{3}$$

$$\begin{aligned} \frac{d\lambda_1}{dt} = {} & 2fk_d I + k_p M_0 \frac{1-x}{1+\varepsilon x}\lambda_0 - k_t \lambda_0 \lambda_1 - \\ & - \lambda_0 \lambda_1 \varepsilon \frac{1-x}{1+\varepsilon x}(k_p + k_{tm}) - k_{tm} M_0 \frac{1-x}{1+\varepsilon x}(\lambda_1 - \lambda_0) \end{aligned} \tag{4}$$

$$\begin{aligned} \frac{d\lambda_2}{dt} = {} & 2fk_d I + k_p M_0 \frac{1-x}{1+\varepsilon x}(2\lambda_1 + \lambda_0) - k_t \lambda_0 \lambda_2 - \\ & - \lambda_2 \lambda_0 \varepsilon \frac{1-x}{1+\varepsilon x}(k_p + k_{tm}) - k_{tm} M_0 \frac{1-x}{1+\varepsilon x}(\lambda_2 - \lambda_0) \end{aligned} \tag{5}$$

$$\frac{d\mu_0}{dt} = k_t \lambda_0^2 - \mu_0 \lambda_0 \varepsilon \frac{1-x}{1+\varepsilon x}(k_p + k_{tm}) + k_{tm} M_0 \frac{1-x}{1+\varepsilon x}\lambda_0 \tag{6}$$

$$\frac{d\mu_1}{dt} = k_t \lambda_0 \lambda_1 - \mu_1 \lambda_0 \varepsilon \frac{1-x}{1+\varepsilon x}(k_p + k_{tm}) + k_{tm} M_0 \frac{1-x}{1+\varepsilon x}\lambda_1 \tag{7}$$

$$\frac{d\mu_2}{dt} = k_t \lambda_0 \lambda_2 - \mu_2 \lambda_0 \varepsilon \frac{1-x}{1+\varepsilon x}(k_p + k_{tm}) + k_{tm} M_0 \frac{1-x}{1+\varepsilon x}\lambda_2 \tag{8}$$

It is assumed that no monomer is consumed in the initiation process and that the quasi-steady-state approximation for the initiator fragment balance is also valid. The ε is a parameter accounting for the volume variation during polymerization and t represents time.

To quantify the gel and glass effects, the following dependencies are proposed:

$$k_t = k_{t0} \exp(A_0 + A_1 \cdot x + A_2 \cdot x^2 + A_3 \cdot x^3) \tag{9}$$

$$k_p = k_{p0} \exp(B_0 + B_1 \cdot x + B_2 \cdot x^2 + B_3 \cdot x^3) \tag{10}$$

where k_{t0} and k_{p0} are the rate constants for termination and propagation reactions in the absence of gel and glass effects and A_0, A_1, A_2, A_3, B_0, B_1, B_2 and B_3 are empirical constants.

For the rate constant of the chain transfer to monomer, a similar decrease to that of propagation rate constant was proposed [7] because both reactions involve the same diffusion mechanism – the monomer molecules migrating toward the growing macroradicals.

$$k_{tm} = k_{tm0} \frac{k_p}{k_{p0}} \tag{11}$$

The empirical parameters depend on initial concentration of the initiator, I_0, and temperature (T) and can be determined by minimizing the least square errors between experimental conversion data and model predictions [8].

By automatic processing of numerous experimental data [9-12], the best correlations between empirical coefficients of the models (9) and (10) and parameters T and I_0 are obtained.

$$\begin{aligned} A, B = {} & a + \frac{b}{T} + c \cdot I_0 + \frac{d}{T^2} + e \cdot I_0^2 + f \cdot \frac{I_0}{T} + \frac{g}{T^3} + \\ & + h \cdot I_0^3 + i \cdot \frac{I_0^2}{T} + j \cdot \frac{I_0}{T^2} \end{aligned} \tag{12}$$

Table 1 Numerical values of constants in gel and glass effect models

	A_0	A_1	A_2	A_3	B_0	B_1	B_2	B_3
a	6671.494	-62659.663	143947.312	-83550.066	5216.517	-5143.078	115683.384	-65355.732
b	-109.433	-0.674	2549.132	-3015.263	-85.750	-47.281	2399.339	-2798.386
c	-59.575	574.171	-1355.835	809.742	-46.544	471.286	-1092.004	637.698
d	0.983	12.599	-87.026	86.865	0.954	13.722	-91.356	91.571
e	0.177	-1.749	4.226	-2.583	0.138	-1.434	3.409	-2.045
f	0.658	-0.535	-12.439	15.375	0.514	-0.307	-11.475	14.038
g	-0.0688	0.588	-1.276	0.754	-0.0257	-0.151	1.264	-1.268
h	-0.000175	0.00177	-0.00436	0.00271	-0.000137	0.00145	-0.00353	0.00216
i	-0.001009	0.0018	0.0140	-0.0188	-0.000774	0.00126	0.0134	-0.0174
j	-0.000937	-0.0551	0.295	-0.278	-0.0022	-0.0338	0.225	-0.226
corr	0.976	0.981	0.974	0.974	0.961	0.969	0.974	0.977

Table 1 contains numerical values for the constants appearing in relations (12). The parameter *corr* shows the agreement with experimental data.

The kinetic model associated with gel and glass effects models were rigorously verified by comparing simulation results with experimental data [13].

For the model of MMA polymerization one considers:

- the state variable vector

  $\overline{z}$ = [I x λ0 λ1 λ2 μ0 μ1 μ2]T =

  = [z1, z2, z3, z4, z5, z6, z7, z8]T (13)

- the model output vector containing numerical and gravimetrical average polymerization degrees

  $\overline{y}$ = [DPn, DPw]T = [y1, y2]T (14)

- the vector of parameters

  $$\overline{p} = \left[T, f, \varepsilon, k_d^0, k_{t0}^0, k_{p0}^0, k_{tm0}^0, E_d, E_t, E_p, E_{tm}\right]^T =$$

  $$[p_1, p_2, p_3, p_4, p_5, p_6, p_7, p_8, p_9, p_{10}, p_{11}]^T \qquad (15)$$

  It should be noted that the reaction temperature, T, is an important operating parameter. Even the model describes satisfactory the evolution of MMA polymerization, establishing of numerical values of kinetic parameters by experimental techniques may be influenced by uncertainties. Therefore, it is necessary to determine the influence of these uncertainties on the model results.

The parametric sensitivity calculus

The parametric sensitivity matrix of the state, $\overline{\overline{S_p^z}}$, has the following components:

$$\overline{\overline{S_p^z}} = \left[S_{p_j}^{z_i}\right] = \begin{bmatrix} S_{p_1}^{z_1} & S_{p_2}^{z_1} & \ldots & S_{p_{11}}^{z_1} \\ S_{p_1}^{z_2} & S_{p_2}^{z_2} & \ldots & S_{p_{11}}^{z_2} \\ \ldots & \ldots & \ldots & \ldots \\ S_{p_1}^{z_8} & S_{p_2}^{z_8} & \ldots & S_{p_{11}}^{z_8} \end{bmatrix} \qquad (16)$$

whose elements are depicted by:

$$S_{p_j}^{z_i}(t) \triangleq \frac{\partial z_i(t)}{\partial p_j} \qquad i = \overline{1,8} \quad j = \overline{1,11} \qquad (17)$$

The matrix $\overline{\overline{S_p^z}}$ can be calculated using the parametric sensitivity equation [14]:

$$\frac{d\overline{\overline{S_p^z}}(t)}{dt} = \overline{\overline{f}}_z(\overline{z}(t), \overline{p}, t) \cdot \overline{\overline{S_p^z}}(t) + \overline{\overline{f}}_p \qquad (18)$$

with the initial condition $\overline{\overline{S_p^z}}(0) = 0$.

In the *Eq.(18)*, $\overline{\overline{f}}_z$ and $\overline{\overline{f}}_p$ are Jacobean matrices of the vector function $\overline{f}(\overline{z}(t), \overline{p}, t)$ with respect to $\overline{z}(t)$ and $\overline{p}$. The components f_1, f_2, ...,f_8 of the vectorial function $\overline{f}(\overline{z}(t), \overline{p}, t)$ are the right members of *Eqs.(1) – (8)*.

The parametric sensitivity matrix of the output, $\overline{\overline{S_p^y}}$, has the form:

$$\overline{\overline{S_p^y}} = \left[S_{p_j}^{y_k}\right] = \begin{bmatrix} S_{p_1}^{y_1} & S_{p_2}^{y_1} & \ldots & S_{p_{11}}^{y_1} \\ S_{p_1}^{y_2} & S_{p_2}^{y_2} & \ldots & S_{p_{11}}^{y_2} \end{bmatrix} \qquad (19)$$

with elements defined by:

$$S_{p_j}^{y_k}(t) \triangleq \frac{\partial y_k(t)}{\partial p_j} \qquad k = \overline{1,2} \quad j = \overline{1,11} \qquad (20)$$

The parametric sensitivity of the output is simply obtained by:

$$\overline{\overline{S_p^y}}(t) = \overline{\overline{g}}_z(\overline{z}(t), \overline{p}, t)) \cdot \overline{\overline{S_p^z}}(t) \qquad (21)$$

with $\overline{\overline{g}}_z$ jacobian matrix of the output vector, $\overline{y}$, with respect to $\overline{z}(t)$.

To compare and order the influence of parameters on system state and output, the dimensionless parametric sensitivity matrices are defined:

$$\overline{\overline{S_p^{*z}}} = \left[S_{p_j}^{*z_i}\right] \triangleq \left[S_{p_j}^{z_i}(t)\frac{p_j}{z_i(t)}\right] \qquad (22)$$

Table 2 Parameters used in MMA polymerization

$k_d^0 = 1.053 \times 10^{15}\ s^{-1}$ (for initiation with AIBN)
$k_{p0}^0 = 4.917 \times 10^2\ m^3/(mol\ s)$
$k_{t0}^0 = 9.8 \times 10^4\ m^3/(mol\ s)$
$k_{tm0}^0 = 4.66 \times 10^6\ m^3/(mol\ s)$
$E_d = 1.2845 \times 10^5$ J/mol
$E_p = 1.822 \times 10^4$ J/mol
$E_t = 2.937 \times 10^3$ J/mol
$E_{tm} = 7.428 \times 10^4$ J/mol
f = 0.58 (AIBN)
$\varepsilon = -(0.1946 + 0.16 \times 10^{-3} \times T\ [°C])$
$k_d = k_d^0 \exp(-E_d/(RT))$
$k_{t0} = k_{t0}^0 \exp(-E_t/(RT))$
$k_{p0} = k_{p0}^0 \exp(-E_p/(RT))$
$k_{tm0} = k_{tm0}^0 \exp(-E_{tm}/(RT))$

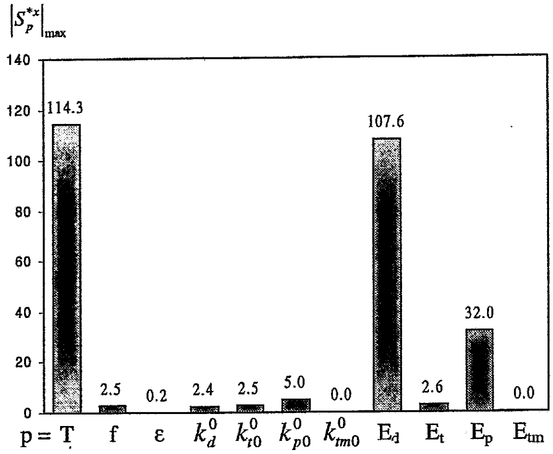

Fig.1 The histogram of maximum absolute values, $\left|S_p^{*x}\right|_{max}$, showing the influence of parameters on monomer conversion

Table 3 Maximum absolute values $\left|S_p^{*z}\right|_{max}$

Parameter	State variables (z)							
(p)	I	x	λ_0	λ_1	λ_2	μ_0	μ_1	μ_2
T	32.6	114.3	951.0	1017.5	1237.5	35.5	130.1	313.5
E_d	31.7	107.6	903.9	945.3	1109.5	35.5	122.9	291.2
E_p	6.2	32.0	269.0	277.4	326.5	10.7	36.6	86.9

$$\overline{\overline{S_p^{*y}}} = \left[S_{p_j}^{*y_k}\right] \underline{\underline{\Delta}} \left[S_{p_j}^{y_k}(t)\frac{p_j}{y_k(t)}\right] \qquad (23)$$

Results and Discussions

Many simulations were made [13] with the model (1) – (12) using a Matlab program based on special functions for solving stiff differential equations. Numerical values of the parameters in kinetic model are given in *Table 2*.

The calculus of the parametric sensitivity functions requires the integration of the mathematical model (*Eqs. (1) – (12)*) and the sensitivity equations (18) for the parametric sensitivity of the system state. The calculus of parametric sensitivity of the system output is performed with *Eq.(21)*.

The integration was carried out directly with *ode15s* in Matlab 5.3, using 10^{-10} as relative and 10^{-15} as absolute tolerances.

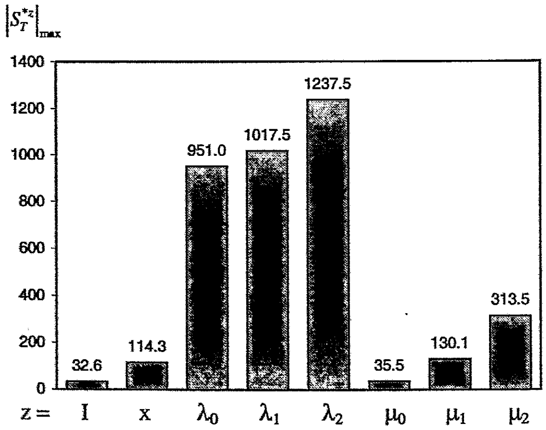

Fig.2 The histogram of maximum absolute values, $\left|S_T^{*z}\right|_{max}$, showing the influence of temperature on state variables

The parametric sensitivity of the state

The histograms of maximal absolute values of the dimensionless (normalized) parametric sensitivity functions of the states indicate the measure in which the parameter variations influence the state variables. All the eight diagrams corresponding to the eight state variables have the same shape, but different values. One of them - the influence of parameters on monomer conversion – is given in *Fig.1*. The parameters with greatest influence on the state variables are: T, E_d and E_p, the maximum absolute values of the dimensionless parametric sensitivities being given in *Table 3*.

Generally, among the parameters, the temperature has the strongest influence and the most sensitive of the state variables are the macroradical concentrations, λ_0, λ_1, λ_2. A suggestive diagram (*Fig.2*) contains the variation domains of the state dimensionless sensitivities as function on temperature.

In conclusion, one should take great care choosing the values of E_d and E_p in different engineering studies of polymerization processes. Also, the thermal regime have to be carefully handled, that means it is necessary the stabilization of the temperature with a good control system.

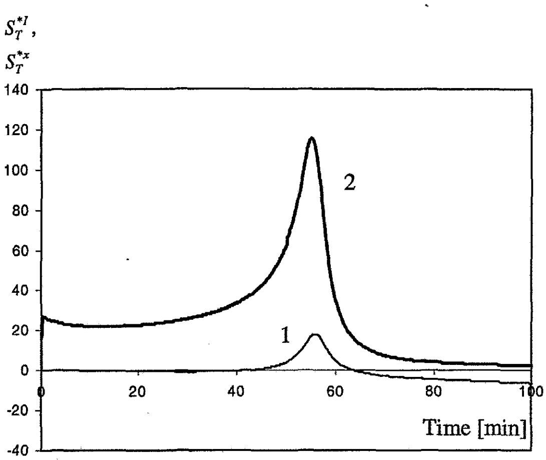

Fig.3 The variation in time of sensitivity functions S_T^{*I} (1), S_T^{*x} (2)

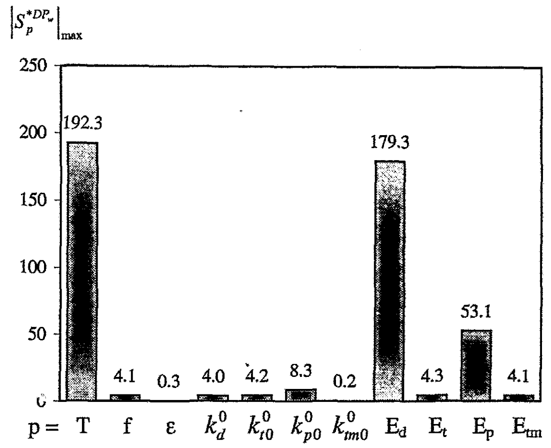

Fig.4 The histogram of maximum absolute values $\left|S_p^{*DP_w}\right|_{\max}$ showing the influence of parameters on gravimetrical average polymerization degree

From the sensitivities presented in *Fig.2* we extracted some of them that have significant non-dimensional values. Thus, *Fig.3* allows to compare the influence of temperature on the initiator concentration and monomer conversion on the whole time interval of the reaction. The greatest influence of temperature corresponds to the gel effect for the both curves and it is more important for monomer conversion (curve 2 in *Fig.3*).

Concerning to the shape of curves representing the dimensional sensitivity functions, S_p^z, we can separate the following categories:

- Diagrams with a positive maximum at the gel effect (about 55 min at T = 70°C and I_0 = 25.8 mol/m^3) representing an increase of the state z when the parameter p increases. Generally, the positive values of the sensitivity functions S_p^z show that increasing the parameter p results in increasing the state z. Such curves are: S_T^I, S_T^x, $S_T^{\lambda_0}$, $S_T^{\lambda_1}$, $S_T^{\lambda_2}$, $S_T^{\mu_1}$, $S_T^{\mu_2}$, S_f^I, S_f^x, $S_f^{\lambda_1}$, $S_f^{\lambda_2}$, $S_f^{\mu_1}$, $S_f^{\mu_2}$, $S_{k_d^0}^I$, $S_{k_d^0}^x$, $S_{k_d^0}^{\lambda_1}$, $S_{k_d^0}^{\lambda_2}$, $S_{k_d^0}^{\mu_1}$, $S_{k_d^0}^{\mu_2}$, $S_{k_{p0}^0}^I$, $S_{k_{p0}^0}^x$, $S_{k_{p0}^0}^{\lambda_1}$, $S_{k_{p0}^0}^{\lambda_2}$, $S_{k_{p0}^0}^{\mu_0}$, $S_{k_{p0}^0}^{\mu_1}$, $S_{k_{p0}^0}^{\mu_2}$, $S_{k_{tm0}^0}^I$, $S_{k_{tm0}^0}^x$, $S_{k_{tm0}^0}^{\mu_1}$, $S_{E_t}^I$, $S_{E_t}^x$, $S_{E_t}^{\lambda_1}$, $S_{E_t}^{\lambda_2}$, $S_{E_t}^{\mu_0}$, $S_{E_t}^{\mu_1}$, $S_{E_t}^{\mu_2}$, $S_{E_{tm}}^{\lambda_1}$, $S_{E_{tm}}^{\lambda_2}$.
- Diagrams with a negative minimum at the gel effect, showing the decrease of the state value, z, when parameter p increases: $S_{E_d}^I$, $S_{E_d}^x$, $S_{E_d}^{\lambda_1}$, $S_{E_d}^{\lambda_2}$, $S_{E_d}^{\mu_1}$, $S_{E_d}^{\mu_2}$, $S_{E_p}^I$, $S_{E_p}^x$, $S_{E_p}^{\lambda_1}$, $S_{E_p}^{\lambda_2}$, $S_{E_p}^{\mu_0}$, $S_{E_p}^{\mu_1}$, $S_{E_p}^{\mu_2}$, S_ε^x, $S_\varepsilon^{\lambda_1}$, $S_\varepsilon^{\lambda_2}$, $S_{k_{t0}^0}^I$, $S_{k_{t0}^0}^x$, $S_{k_{t0}^0}^{\lambda_1}$, $S_{k_{t0}^0}^{\lambda_2}$, $S_{k_{t0}^0}^{\mu_0}$, $S_{k_{t0}^0}^{\mu_1}$, $S_{k_{t0}^0}^{\mu_2}$, $S_{k_{tm0}^0}^{\lambda_1}$, $S_{k_{tm0}^0}^{\lambda_2}$, $S_{E_{tm}}^I$, $S_{E_{tm}}^x$, $S_{E_{tm}}^{\mu_1}$.

For two above categories of curves, the domains before and after gel effect are characterized by a zero or weak parameter influence, positive or negative.

A distinct category of curve shows a positive maximum or a negative minimum at the gel effect and this influence remains approximately constant after this phenomenon. Such curves are: $S_{k_{p0}^0}^{\lambda_0}$, $S_{k_{tm0}^0}^{\lambda_0}$, $S_{E_{tm}}^{\mu_2}$ and $S_{E_p}^{\lambda_0}$, S_ε^I, $S_\varepsilon^{\mu_1}$, $S_\varepsilon^{\mu_2}$, $S_{k_{tm0}^0}^{\mu_2}$, $S_{E_{tm}}^{\lambda_0}$, respectively.

A limited group of curves illustrates a continuous positive increasing influence ($S_T^{\mu_0}$, $S_f^{\lambda_0}$, $S_f^{\mu_0}$, $S_{k_d^0}^{\lambda_0}$, $S_{k_d^0}^{\mu_0}$, $S_{k_{tm0}^0}^{\mu_0}$, $S_{E_t}^{\lambda_0}$) or continuous negative decreasing influence ($S_{E_d}^{\lambda_0}$, $S_{E_d}^{\mu_0}$, $S_\varepsilon^{\lambda_0}$, $S_\varepsilon^{\mu_0}$, $S_{k_{t0}^0}^{\lambda_0}$, $S_{E_{tm}}^{\mu_0}$). Yet, an increased influence at the gel effect is observed.

The majority of curves shows zero influence of the parameters before the gel effect, the critical domain is represented by the gel effect and after this phenomenon the influence may be strong (as to the gel effect) or weak.

The parametric sensitivity of the output

The maximal absolute values of the dimensionless parametric sensitivities of the output show the influence of the parameter variations on the model output, DP_n and DP_w. The *Fig.4* emphasizes that the most important parameters for DP_w are T, E_d and E_p, the same as in the case of parametric sensitivity of the state. Qualitatively, the results obtained for DP_w are also valid for DP_n, numerical values of the sensitivities being different.

The parameters T, E_d and E_p have a major influence on DP_n and DP_w in the gel effect region. This influence is positive for T and negative for E_d and E_p. Before and after the gel effect, the negative values of the $S_T^{DP_n}$ and $S_T^{DP_w}$ mean that an increase of temperature results in a decrease of polymerization degrees, while in the gel effect domain the action of temperature is opposite (*Fig.5*). A positive variation of E_d produces a decrease of DP_n and DP_w at the gel effect moment and an increase of these outputs in other time intervals of the reaction. The negative values of $S_{E_p}^{DP_n}$ and $S_{E_p}^{DP_w}$ prove that the increase of E_p produces the decrease of the polymerization degrees on the entire time domain, with the greatest decrease at the gel effect moment.

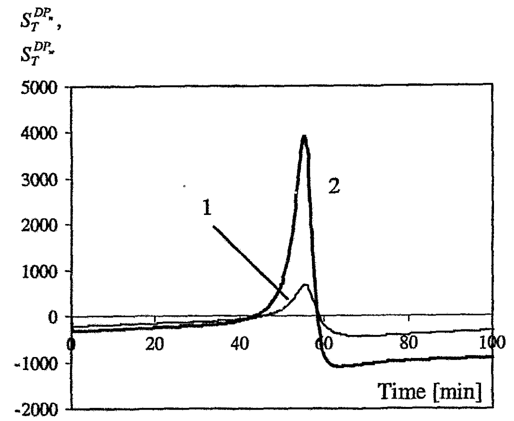

Fig.5 The variation in time of sensitivity functions $S_T^{DP_n}$ (1), $S_T^{DP_w}$ (2)

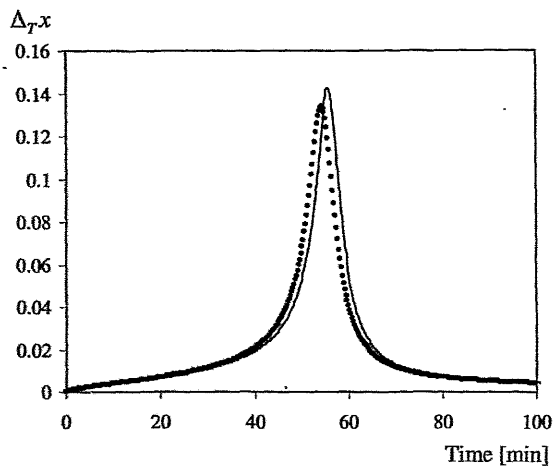

Fig.6 The conversion variation caused by temperature increase; solid line - calculus based on sensitivity functions; dotted line - calculus based on model simulations

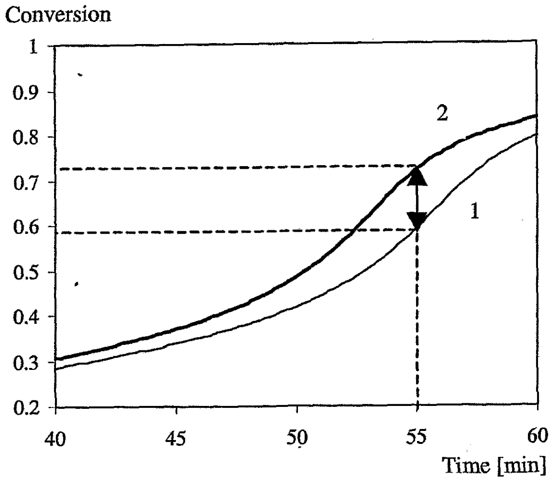

Fig.7 The influence of temperature increase on monomer conversion; 1 - initial conversion; 2 - disturbed conversion caused by temperature change

The quantitative estimation of the parameter influence on the system states and outputs

With the addition of sensitivity functions there were calculated the deviation of the states z when each "p" parameter changes:

$$\Delta_p z = S_p^z \cdot \Delta p \qquad (24)$$

Similar for the system outputs ($\Delta_p y = S_p^y \cdot \Delta p$).

The first example of using sensitivity functions involves a small variation of temperature, 0.2% (about 0.7°C, respectively). *Fig.6* shows the conversion variation caused by temperature change ($\Delta_T x$) calculated with sensitivity functions (solid line): $\Delta_T x = S_T^x \cdot \Delta T$ and by model simulation (dotted line). The good agreement between the two curves in *Fig.6* illustrates the correctness of the sensitivity function values. Consequently, these functions can be used to provide quantitative information about the polymerization system. The maximum value of the curves in *Fig.6* (0.15) means that a temperature increase of 0.2% at t = 55 min (gel effect) determines a conversion increase of 0.15. This is clearly emphasized in *Fig.7* where curve noted 1 represents the initial conversion, and curve 2 is the conversion resulted with temperature change.

For the simultaneous variation of the three parameters with greatest influence on the states - T, E_d, E_p - with variations of 0.2%, -0.1%, 0.6%, a conversion increase of 0.4 at the gel effect and a decrease of this state of 0.6 at the end of the reaction take place.

For the most sensitive parameters - T, E_d, E_p - very small changes have been considered. Because of strong nonlinear model of the polymerization process in connection with T, E_p E_d, we cannot appreciate quantitatively the influence of these parameters if their changes are greater. But, the sensitivity functions offer important qualitative information.

The temperature is one of the parameters with significant influence on polymerization degrees - the outputs of the polymerization system under study. An increase of temperature with 0.2% determines an initial decrease of polymerization degrees, followed by an important increase at the gel effect moment (approximately with 450 units for DP_n and 2700 units for DP_w). Greater values of polymerization degrees mean, in fact, earlier appearance of the gel effect due to the temperature increase. After the gel effect, the increase of temperature results the decrease of polymerization degrees with 300 units for DP_n and approximately 700 units for DP_w.

The following example involves a variation of 2% for the parameter ε. This change of ε parameter determines an increase of polymerization degrees of 1100 units, approximately, for DP_n (*Figs.8* and *9*) and 5800 for DP_w

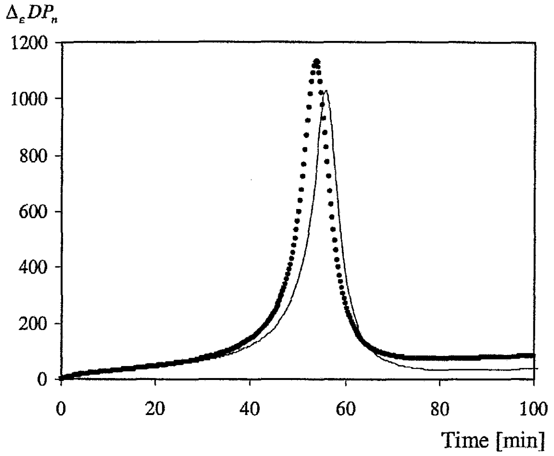

Fig.8 The variation of numerical average polymerization degree caused by ε parameter change; solid line - calculus based on sensitivity functions; dotted line - calculus based on model simulations

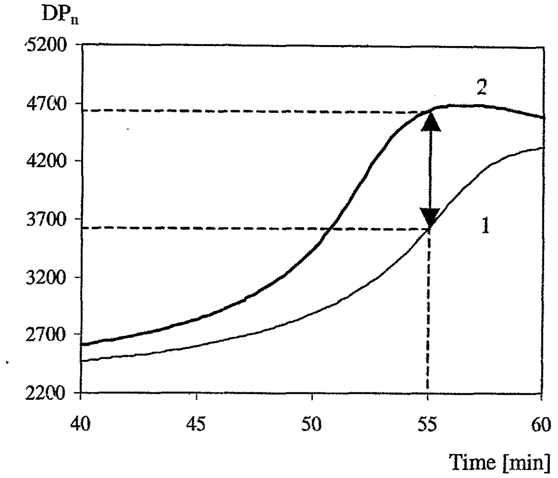

Fig.9 The influence of ε parameter change on numerical average polymerization degree; 1 - initial DP_n; 2 - disturbed DP_n

Conclusions

This paper is dealing with parametric sensitivity of isothermal batch bulk polymerization of methyl methacrylate. The kinetic model including the mathematical relations for diffusion controlled phenomena describes quite well the polymerization process, continuously on the whole conversion domain and for different reaction conditions. The termination and propagation rate constants dependencies of monomer conversion, initial initiator concentration and temperature are the suitable form for the sensitivity analysis.

The sensitivities of the state variables (initiator concentration, monomer conversion and distribution moments of the chain length) and the model outputs (numerical and gravimetrical polymerization degrees) with respect to various parameters (temperature, initiator efficiency, volume variation parameter, frequency factors, activation energies) are computed. It is found that the temperature has the strongest influence on the state and output of the polymerization system. Therefore, the thermal regime of the reactor have to be carefully controlled. Other two parameters influencing significantly the polymerization process are the propagation and initiation activation energies. Consequently, it is important to have precise estimation of these two parameters for good design and operation of the reactor.

Generally, diagrams of parametric sensitivities show a positive maximum or a negative minimum representing an increase or a decrease of the system variables when the considered parameter increases. These values represent the generalized sensitivity boundaries for reactor design or operation and correspond to the gel effect.

A calculus based on sensitivity functions are used to made quantitative estimations of the parameter influence on the system state and output variables. For the most sensitive parameters – temperature, initiation and propagation activation energies – very small changes have been considered. The sensitivity analysis method cannot be used to appreciate the changes of the system variables at greater variations of the most sensitive parameters because the kinetic model is strongly nonlinear.

REFERENCES

1. BIESENBERGER J. A.: Am. Chem. Soc. Symp. Ser. *1979*, 104, 15.
2. BAILLAGOU P. E. and SOONG D. S.: Chem. Eng. Sci., *1985*, 40, 75.
3. BAILLAGOU P. E. and SOONG D. S.: Chem. Eng. Sci., *1985*, 40, 87.
4. TJAHJADI M., GUPTA S. K., MORBIDELLY M. and VARMA A.: Chem. Eng. Sci., *1987*, 42, 2385.
5. KAPOOR B., GUPTA S. K. and VARMA A.: Polym. Eng. Sci., *1989*, 18, 1246.
6. CHIU W. Y., CARRATT G. M. and SOONG D. S.: Macromolecules, *1983*, 16, 348.
7. VAID N. R. and GUPTA S. K.: Polym. Eng. Sci., *1991*, 31(2), 1708.
8. CURTEANU S., BULACOVSCHI V. and LISA C.: Polym. Plast. Technol. Eng., *1999*, 38 (5), 1121.
9. BALKE T. S. and HAMIELEC A. E.: J. Appl. Polym. Sci., *1973*, 17, 905.
10. ITO K. J.: J. Polym. Sci., Part A-1, *1989*, 13, 401.
11. DUA V., SARAF D. N. and GUPTA S. K.: Polym. Eng. Sci., *1996*, 59, 749.
12. CURTEANU S. and CAZACU M., Rev. Chim., in press.
13. CURTEANU S., PETRILA C. and BULACOVSCHI V.: Rev. Roum. Chim., in press.
14. UNGUREANU S.: Sensibilitatea sistemelor dinamice, Ed. Tehnică, Bucureşti, pp. 45, 1988.