Free Radical Polymerization of Methyl Methacrylate: Modeling and Simulation under Semibatch and Nonisothermal Reactor Conditions

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ABSTRACT: For the bulk free radical polymerization of methyl methacrylate (MMA), equations of the material balance can be written that are based on a kinetic diagram that considers initiation by decomposition of an AIBN initiator, propagation, and termination by disproportionation. To quantify the gel and glass effects simple empirical dependences are used between the rate constants of termination and propagation and monomer conversion. Numerical values for the empirical parameters at different temperatures and initiator concentrations are also given. Conversion history and molecular weights are obtained by simulation when an initiator or monomer are added to the reaction mass and the temperature modifies after some reaction has taken place. These intermediate operations are simulated at different moments with respect to the gel and glass effects. The validation of the model for semibatch and nonisothermal conditions are made by comparing the simulation results with literature experimental data. The most important conclusion of the article is that the empirical model proposed for the gel and glass effects can be successfully used under semibatch and nonisothermal reactor conditions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2561–2570, 1999

Key words: free radical polymerization; methyl methacrylate; gel and glass effects; semibatch and nonisothermal reactor conditions

INTRODUCTION

A major feature of homogeneous free radical polymerization is the important increase of the mass reaction viscosity with monomer conversion. In these conditions one can observe a deviation from the "normal" kinetic and significant changes of mass and heat transfer.

Most sensitive to the increase of viscosity is the termination rate constant, k_t. The severe reduction in the mobility of macroradicals introduces a decrease of k_t values, resulting in an autoacceleration of the reaction and an increase of the polymerization degree (gel effect or Trommsdorff effect).

Usually, when the polymerization is carried out at lower temperatures, a transition state might be reached at a certain conversion, which means that the polymerization temperature equals the glass transition of the polymer–monomer mixture (glass effect). Under such conditions the propagation rate constant decreases, causing the interruption of the reaction before the monomer is completely consumed.

One should note that the propagation rate constant is less sensitive to the diffusion because of the mobility of the monomer molecules. On the other hand, because of the increased viscosity at high monomer conversion, the initiator efficiency decreases (the so-called cage effect).

In order to quantitatively describe these complex effects, the mathematical model expressions should reflect the variation of the rate constants of the reactions controlled by diffusion, k_t and k_p.

The literature in the last few years mentions many improved models for the diffusion effects in free radical polymerization. Their purpose is to obtain a good agreement between experimental reality and models based on molecular theories, as well as the possibility of using these models for engineering applications such as sensitivity analysis, optimal parameter estimation, optimal control, and so forth.

The first approaches for the gel and glass effects modeling have used simple empirical methods to correlate the apparent rate constant with different parameters of the system like conversion, temperature, and free volume.[1,2] Subsequently, efforts have been made to ground the models on a molecular basis using different theories of diffusion phenomena.[3–9] Many of these attempts have considered diffusional restrictions on the rate constants, so interrupting points did appear.

A big gain for the engineering of the polymerization reaction is the Chiu et al. model,[10] which is a phenomenological model based on the Fujita–Doolitle free volume theory.[11] Diffusional limitations were introduced as an integral part of the termination and propagation reactions, and the effects of composition, temperature, and molecular weight accounted for continuity.

Grounding the modeling of diffusion phenomena on a molecular basis assumes the reduction of the number of empirical parameters. Still, their presence in the model makes the fitting of the simulation data to the experimental data easier. Thus, the model appears to be more flexible. In other words, the improvements do not involve the elimination of the adjustable parameters.

Louie and Song[12,13] used the Chiu et al. model[10] for simulation and optimization of semibatch reactors. Their results are doubtful because the model uses the initial concentration of the initiator to account for the dependence of the polymer radicals' diffusivity on the molecular weight.

Achilias and Kiparissides[14,15] did extend the Chiu et al. model[10] using the diffusion theory of Vrentas and Duda[16] and the theory of excess chain-end mobility.[17] They applied this model to semibatch reactors and to reactors operating under nonisothermal conditions. A controversy arises in the use of an empirical curve-fit parameter correlated to the initial numeric average chain length.
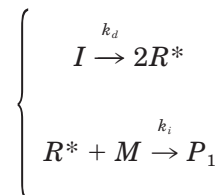
Saraf et al.[3,4,18,19] developed a general model using the free volume theory of Vrentas and Duda[16] and simplified the expressions of the rate constants according to Chiu et al.'s method.[10] In order to quantify the gel, glass, and cage effects, the model uses three parameters θ_t, θ_p, and θ_f. It is worth mentioning that it is the only model that was successfully applied to the semibatch and nonisothermal reactors.

The goal of this article is to demonstrate the possibility of using a simple empirical model to describe semibatch and nonisothermal reactor conditions with good results.
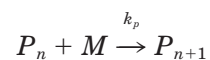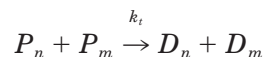
EXPERIMENTAL

Kinetic Model

For initiated free radical polymerization of methyl methacrylate (MMA) in a homogeneous system, the following kinetic diagram is considered: initiation is

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

propagation is

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

termination by disproportionation is

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

where I, M, and R^* denote the initiator, monomer, and primary radical, respectively; P_n and D_n represent the macroradical and the dead polymer with n monomer units, respectively; and k_d, k_i, k_p, and k_t are rate constants for initiator decomposition, initiation, propagation, and termination, respectively.

Based on a kinetic diagram, one can write the material balance equations for monomer conver-

Table I Parameters Used in Gel and Glass Effects Models for MMA Polymerization in Isothermal Batch Reactors

Temp. (°C)	Initiator Concn. (mol/L)	A_1	A_2	A_3	A_4	B_1	B_2	B_3	B_4
50	0.01548	−0.39	5.00	−48.32	22.20	0.11	−2.81	14.25	−18.45
50	0.0258	−0.33	5.00	−39.52	12.23	0.31	−6.92	31.57	−36.45
60	0.0258	−0.21	3.76	−25.37	0.39	0.47	−9.43	39.58	−42.28
70	0.01548	−0.23	3.00	−22.83	−0.95	0.50	−9.53	38.32	−39.55
70	0.0258	−0.39	6.31	−27.51	1.78	0.42	−8.20	33.92	−36.52
80	0.0258	−1.36	18.72	−56.99	22.28	−0.21	0.91	5.65	−14.78

sion (x), concentration of the initiator (I), and moments of radicals (λ_k) and dead polymer $(\mu_k, k = 0, 1, 2)$, which give the distribution of the chain length:

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

$$\frac{dx}{dt} = k_p(1-x)\lambda_0 \quad (2)$$

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

$$\frac{d\lambda_1}{dt} = k_p M_0 \frac{1-x}{1+\varepsilon x} \lambda_0 - k_t \lambda_0 \lambda_1 - \lambda_0 \lambda_1 \varepsilon \frac{1-x}{1+\varepsilon x} k_p \quad (4)$$

$$\frac{d\lambda_2}{dt} = k_p M_0 \frac{1-x}{1+\varepsilon x} (2\lambda_1 + \lambda_0) - k_t \lambda_0 \lambda_2$$
$$- \lambda_2 \lambda_0 \varepsilon \frac{1-x}{1+\varepsilon x} k_p \quad (5)$$

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

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

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

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 ac-

counting for the volume variation occurring during polymerization as a function of temperature in accordance with[20]

$$\varepsilon = -[0.1946 + 0.916 \times 10^{-3} \times T \text{ (°C)}] \quad (9)$$

The following initial conditions should be attached to the model: $I(0) = I_0$, $M(0) = M_0$, $\lambda_k(0) = 0$, and $\mu_k(0) = 0$. In eqs. (1)–(8) t represents time.

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

$$k_t = k_{t0}\exp(A_1 + A_2 x + A_3 x^2 + A_4 x^3) \quad (10)$$

$$k_p = k_{p0}\exp(B_1 + B_2 x + B_3 x^2 + B_4 x^3) \quad (11)$$

where k_{t0} and k_{p0} are the rate constants for termination and propagation in the absence of gel and glass effects and A_1, A_2, A_3, A_4, B_1, B_2, B_3, and B_4 are empirical constants. The empirical parameters depend on the initial concentration of the initiator, I_0, and temperature, T. Table I contains these values for different I_0 and T. Parameters in the model were obtained using a curve fit of experimental data on MMA polymerization in isothermal batch reactors.[21]

Numerical values used in the simulation and some computing relations are given in Table II.[10,20,22] In Table II the k_d^0, k_{p0}^0, and k_{t0}^0 are frequency factors for the rate constant of initiator decomposition, propagation, and termination, respectively, in the absence of gel and glass effects; E_d, E_p, and E_t represent activation energies of the initiator decomposition, propagation, and termination, respectively; and f is the initiator efficiency.

Table II Parameters Used in MMA Polymerization

$k_d^0 = 1.053 \times 10^{15}$ s^{-1} (for initiation with AIBN)
$k_{p0}^0 = 4.917 \times 10^5$ L/(mol s)
$k_{t0}^0 = 9.8 \times 10^7$ L/(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
$f = 0.58$ (AIBN)
$k_d = k_d^0 \exp[-E_d/(RT)]$
$k_{t0} = k_{t0}^0 \exp[-E_t/(RT)]$
$k_{p0} = k_{p0}^0 \exp[-E_p/(RT)]$

RESULTS AND DISCUSSION

The model was used to predict the changes of monomer conversion and molecular weights after the intermediate addition of initiator or monomer and after step changes in the temperature while the reaction proceeds. These operations were simulated at different times with respect to gel and glass effects before and during the gel or glass effects.

The simulations were carried out with a program for solving Stiff differential equations of the model. The moment at which an intermediate change takes place represents a breakpoint in the program.

Step changes in temperature at some points during polymerization were considered: a step increase (SI) and a step decrease (SD). Isothermal polymerization of MMA with AIBN was carried out at 70°C with $I_0 = 0.0258$ mol/L (reference curve R). The sudden increase (SI of +10°C) and decrease (SD of −10°C) of the temperature at $t = 26.6$ min ($x = 18.4\%$; i.e., before the gel effect) had a strong influence on the monomer conversion and weight average molecular weight, M_w (Figs. 1, 2). Arrows indicate the time or conversion at which the step change was effected.

The number average molecular weight, M_n, did not suffer essential changes, so this plot was not provided.

At this moment ($t = 26.6$ min, $x = 18.4\%$) the instantaneous increase of temperature makes the gel effect occur earlier as compared to isothermal polymerization (70°C, R curve) because of higher rates associated with such a temperature. As was expected, the decrease of temperature from 70 to 60°C resulted in a later occurrence of the gel effect.

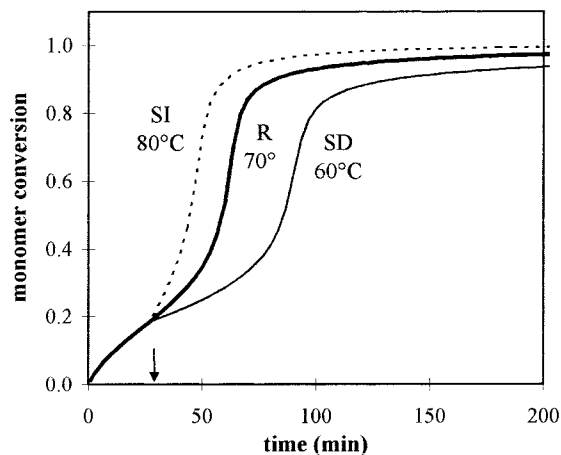During the polymerization processes the high molecular weights are obtained at lower temper-

Figure 1 The influence of instantaneous changes in temperature on monomer conversion before the gel effect; SI, +10°C; SD, −10°C; R, reference curve ($T = 70$°C, $I_0 = 0.0258$ mol/L).

ature. So, as a result of the SI, the molecular weight decreases (Fig. 2). By contrast, the SD yields an increase of the M_w.

If the temperature changes ±10°C at the point $t = 50$ min ($x = 34.7\%$, during the gel effect), similar consequences are obtained; the only difference is that the change of the place for the gel effect is smaller in time (Fig. 3). In exchange, the values of the M_w differ strongly from those corresponding to the isothermal conditions (70°C, Fig. 4).

As a consequence, one should note that a variation of ±10°C determines a meaningful modification of the time to gelation and the M_w.
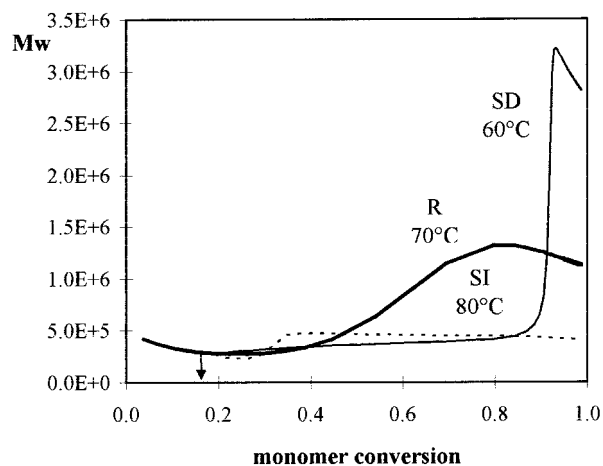

Figure 2 The influence of an instantaneous change in temperature on the gravimetric average molecular weight before the gel effect; SI, +10°C; SD, −10°C; R, reference curve ($T = 70$°C, $I_0 = 0.0258$ mol/L).
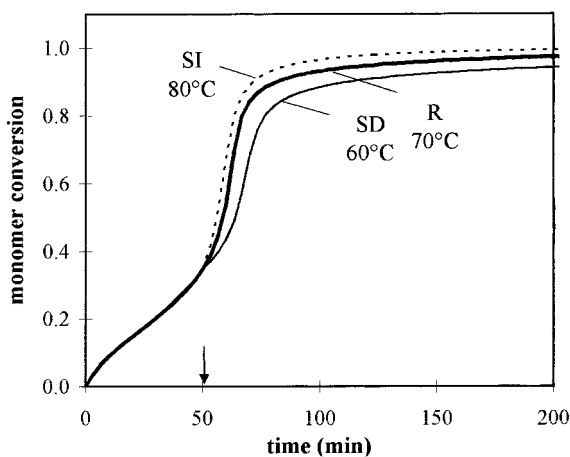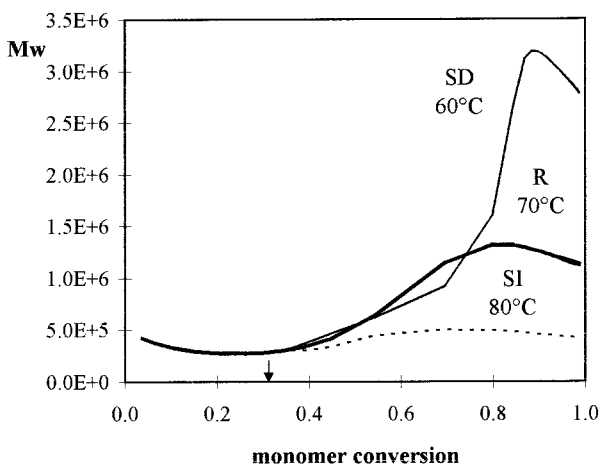
Figure 3 The influence of an instantaneous change in temperature on the monomer conversion during the gel effect; SI, +10°C; SD, −10°C; R, reference curve (T = 70°C, I_0 = 0.0258 mol/L).
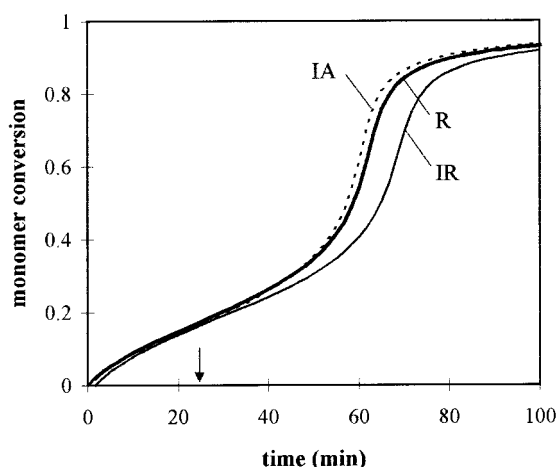

Figure 5 The influence of the addition (IA) or removal (IR) of initiator on the monomer conversion before the gel effect; R, initial conversion (T = 70°C, I_0 = 0.0258 mol/L); IA, +0.005 mol/L; IR, −0.005 mol/L.

Intermediate Modification of Initiator Amount

If one considers an instantaneous adding (IA) or removal (IR) of 0.005 mol/L AIBN at t = 25 min (x = 17.5%) and T = 70°C, the gel effect occurs earlier (IA) or later (IR; Fig. 5) and the obtained molecular weights are lower (IA) or higher (IR; Fig. 6) compared to previous conditions (reference curve R: I_0 = 0.0258 mol/L, T = 70°C).

Negligible changes of conversion and molecular weights are observed when instantaneous addition or removal of the initiator happens during the gel effect. By performing the same operation

during the glass effect, no influence on the polymerization process can be observed. Therefore, the adding of a supplementary amount of initiator before the onset of the gel effect may have important influences on the product properties.

The third aspect of semibatch operating conditions refers to the intermediate addition or removal of the monomer.

The initial conditions for this simulation are T = 70°C, I_0 = 0.0258 mol/L, and M_0 = 9.13 mol/L.

Figure 4 The influence of an instantaneous change in temperature on the gravimetric average molecular weight during the gel effect; SI, +10°C; SD, −10°C; R, reference curve (T = 70°C, I_0 = 0.0258 mol/L).
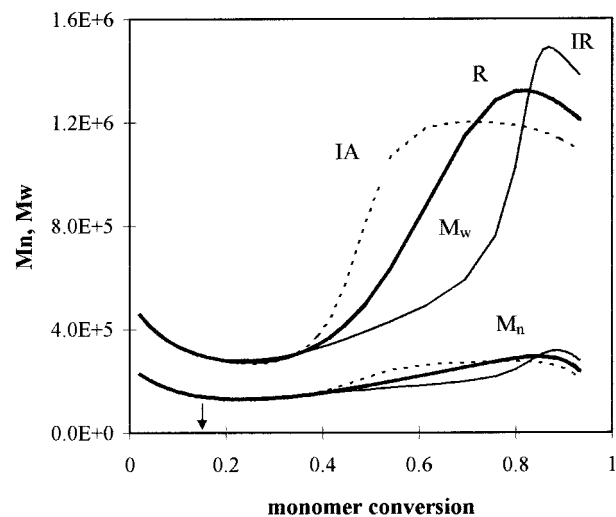

Figure 6 The influence of the addition (IA) or removal (IR) of initiator on the molecular weights before the gel effect; R, reference curve (T = 70°C, I_0 = 0.0258 mol/L); IA, +0.005 mol/L; IR, −0.005 mol/L.
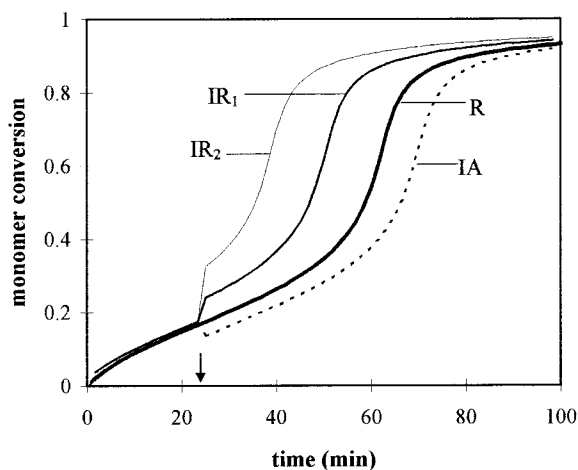
Figure 7 The influence of the addition (IA) or removal (IR$_1$, IR$_2$) of the monomer on the conversion before the gel effect; R, reference curve ($T = 70°C$, $I_0 = 0.0258$ mol/L); IA, +4 mol/L; IR$_1$, −2 mol/L; IR$_2$, −4 mol/L.

At $t = 25$ min ($x = 17.5\%$, region of pregel effect), 4 mol/L of pure monomer are added (IA) or 2 or 4 mol/L monomer are removed (IR$_1$, IR$_2$, respectively). The addition of the monomer determines a sudden drop of the conversion (Fig. 7) because it is calculated with respect to the total amount of the monomer at time t. The gel effect is delayed compared to the reference polymerization (curve R), and this is because the concentration of the polymer is lower.

In Figure 8 one observes that the addition of the monomer before the gel effect causes an increase of the molecular weight, while its removal determines a decrease of the molecular weight.

Figures 9 and 10 point out the influence of the intermediate addition or removal of the monomer during the gel effect ($t = 60$ min, $x = 54\%$) upon the conversion and molecular weights. The conversion first achieves a sudden decrease (IA) or increase (IR$_1$, IR$_2$), which is more pronounced compared to that at $t = 25$ min (Fig. 7). The gel effect appears later (IA) or earlier (IR$_1$, IR$_2$) with respect to the reference polymerization, R. The changes in the molecular weights (Fig. 10) are similar to those discussed in the previous case (Fig. 8).

The addition of the pure monomer during the glass effect has no influence on monomer conversion, while the M_w increases.

In order to obtain polymers with preestablished properties, one should consider the possibility of adding a mixture of monomer and initiator at certain stages during the polymerization.
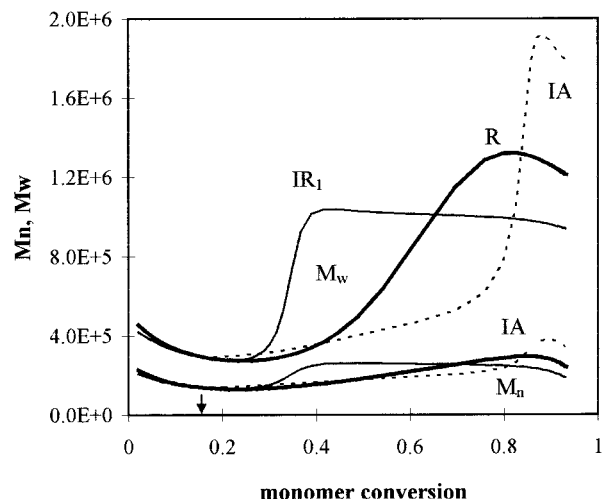

Figure 8 The influence of the addition (IA) or removal (IR$_1$) of the monomer on the molecular weights before the gel effect; R, reference curve ($T = 70°C$, $I_0 = 0.0258$ mol/L); IA, +4 mol/L; IR$_1$, −2 mol/L.

Comparison with Experimental Data

To validate this model for step changes of temperature and for semibatch reactor conditions the experimental data for MMA obtained by Saraf et al.[3,4] were used. The model was examined for step changes in temperature and initiator concentration because these are two important control variables in free radical polymerization systems. These idealized operations are sufficient for
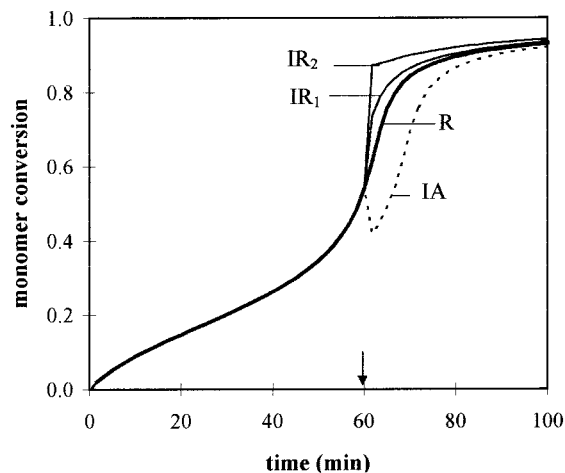

Figure 9 The influence of the addition (IA) or removal (IR$_1$, IR$_2$) of the monomer on the conversion during the gel effect; R, reference curve ($T = 70°C$, $I_0 = 0.0258$ mol/L); IA, +4 mol/L; IR$_1$, −2 mol/L; IR$_2$, −4 mol/L.
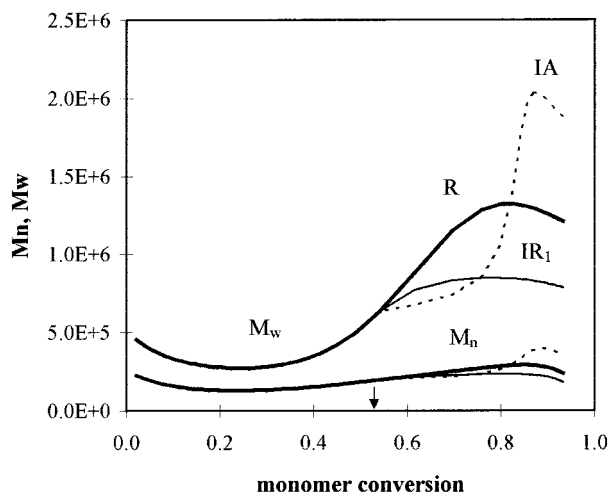
Figure 10 The influence of the addition (IA) or removal (IR_1) of the monomer on the molecular weights during the gel effect; R, reference curve ($T = 70°C$, $I_0 = 0.0258$ mol/L); IA, $+4$ mol/L; IR_1, -2 mol/L.

checking the validity of the model for more general situations.[4]

In order to find out the best agreement between the experimental conversion and molecular weight with model predictions, it was necessary to adjust the empirical parameters in eqs. (10) and (11).

The change of temperature from 70 to 50°C ($I_0 = 0.0258$ mol/L, $t = 26.6$ min, $x = 18\%$) leads to the SD1 dashed curves in Figure 11. The SD1(1) representation was obtained by simulation with values of the parameters taken from Table I (values for batch operating conditions), while the SD1(2) curve was drawn by using adjusted values (Table III) of these parameters.

The adjustment of the A_1, A_2, A_3, A_4, B_1, B_2, B_3, and B_4 quantities was done by using the method of least square error between the experimental data and model predictions according to

$$\min E = \sum_{i=1}^{N_x} \left(\frac{x_i^{\text{exp}} - x_i^{\text{th}}}{x_i^{\text{exp}}} \right)^2 \qquad (12)$$

where the superscripts exp and th indicate the experimental and theoretical values, respectively, and N_x is the number of data points for monomer conversion x_i.

The first column in Table III contains the lettercode identifying the operation that will be checked experimentally (as it was noted in the text), the second column presents the conditions

T and I_0 before the intermediate operation, and the third one refers to the conditions of intermediate instantaneous operation (T, t, and x).

Figure 12 presents a logarithmic scale of the M_w values obtained by the SD1 simulation and experimentally. For this representation the model parameters are taken from Table I.

For a modification of temperature from 70 to 50°C (SD2) at $t = 45$ min ($x = 31.5\%$) one attains the representations in Figures 13 and 14. The SD2(1) curve (Fig. 13) and M_w (Fig. 14) were obtained by taking the parameters given in Table I ($T = 50°C$ and $I_0 = 0.0258$ mol/L). To obtain the SD2(2) curve the A and B values from Table III were used.

An SI of temperature from 50 to 70°C ($t = 120$ min, $x = 15.9\%$) causes the gel effect to occur earlier. The drawn SI(1) curve in these conditions appears to be very close to the experimental data. For drawing the SI(2) curve the empirical parameters were adjusted according to Table III (Fig. 15).

The semibatch experiments were carried out at constant temperatures (50 and 70°C) and an SI in the initiator concentration from about 0.01548 to 0.1 mol/L was done at different reaction times.[1] The simulation results obtained in these conditions are presented in Figures 16–18.

The appropriate A_1, A_2, A_3, A_4, B_1, B_2, B_3, and B_4 values, as well as the simulating conditions in Figures 16–18, are given in Table III and correspond to codes (d–f), respectively.
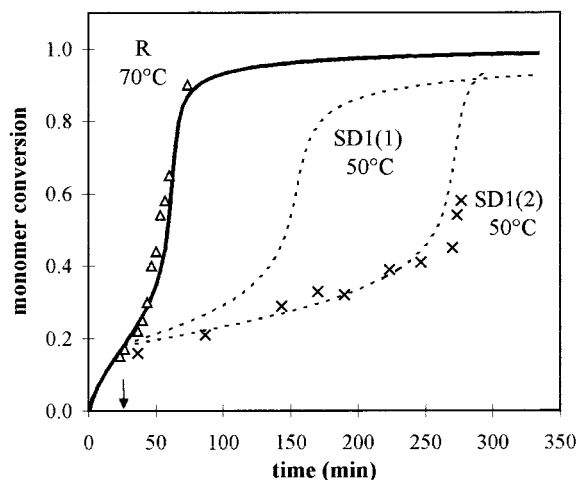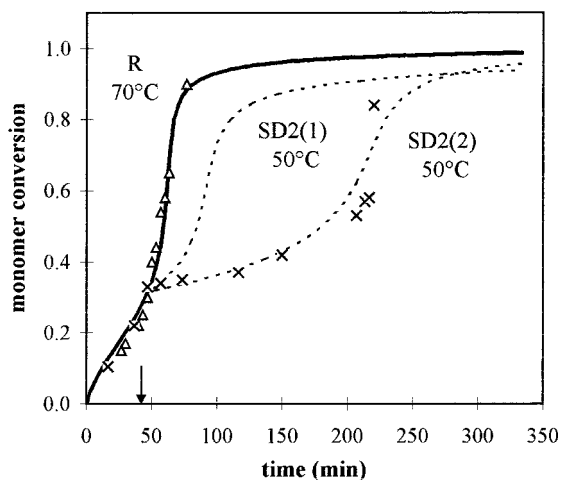

Figure 11 Comparison between model prediction (—, --) and experimental data [($\triangle$) 70°C; SD1, ($\times$) 50°C] concerning monomer conversion for a step decrease of temperature (SD1, from 70 to 50°C) before the gel effect; code (a) in Table III; R, reference curve ($T = 70°C$, $I_0 = 0.0258$ mol/L).

Table III Parameters Used in Polymerization Models of Gel and Glass Effects for Semibatch and Nonisothermal Operating Conditions

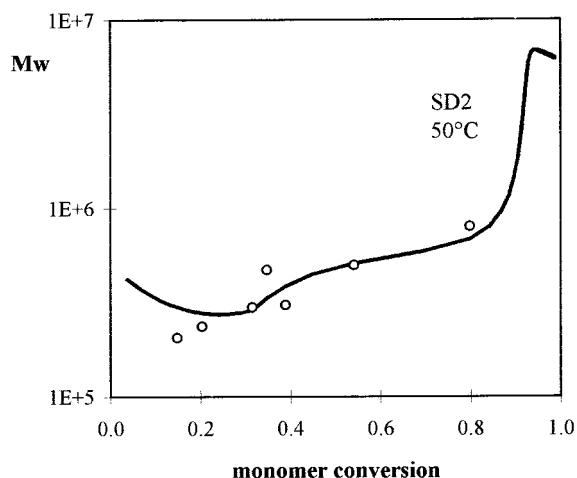| Code	Initial Conditions	Intermediate Operation	B_1	B_2	B_3	B_4	A_1	A_2	A_3	A_4
(a)	$I_0 = 0.0258$ mol/L, $T = 70°C$	SD1: $T = 50°C$, $t = 26.6$ min, $x = 18\%$	0.31	−6.92	31.57	−30	−0.1	11	−39.52	12.23
(b)	$I_0 = 0.0258$ mol/L, $T = 70°C$	SD2: $T = 50°C$, $t = 45$ min, $x = 31.5\%$	0.31	−6.92	31.57	−30	−0.1	14	−39.52	12.23
(c)	$I_0 = 0.0258$ mol/L, $T = 50°C$	SI: $T = 70°C$, $t = 120$ min, $x = 15.9\%$	0.50	−8.20	33.92	−36.52	−0.39	3	−27.51	1.78
(d)	$I_0 = 0.01548$ mol/L, $T = 50°C$	IA1: $I = 0.1$ mol/L, $t = 90$ min, $x = 9.7\%$	0.11	−2.81	14.25	−18.45	−0.39	7	−48.32	22.20
(e)	$I_0 = 0.01548$ mol/L, $T = 50°C$	IA2: $I = 0.1$ mol/L, $t = 170$ min, $x = 17.3\%$	0.11	−2.81	14.25	−18.45	−0.39	6	−48.32	22.20
(f)	$I_0 = 0.01548$ mol/L, $T = 70°C$	IA3: $I = 0.1$ mol/L, $t = 26.6$ min, $x = 15.2\%$	0.50	−9.53	38.32	−39.55	−0.23	6	−22.83	−0.95
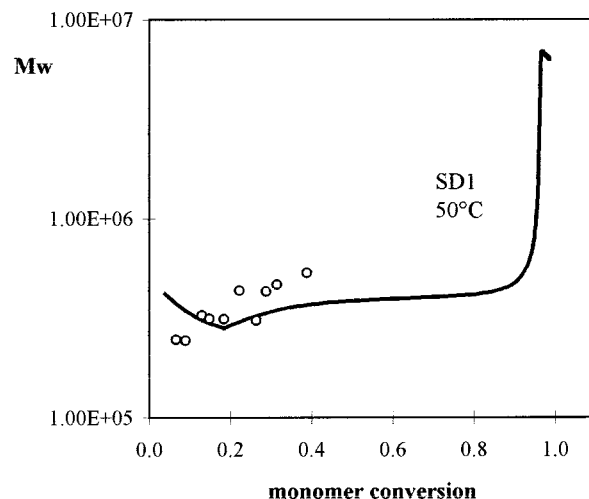
Figure 12 Comparison between (—) model prediction and (○) experimental data concerning the gravimetric molecular weight for a step decrease of temperature (SD1, from 70 to 50°C) before the gel effect.

CONCLUSIONS

Models (1)–(8), (10), and (11) have the following advantages: they are simple, easy to handle, and can be used with good results under batch, semibatch, and continuous reactor conditions, as well as under nonisothermal conditions. The major drawback comes from their empirical character
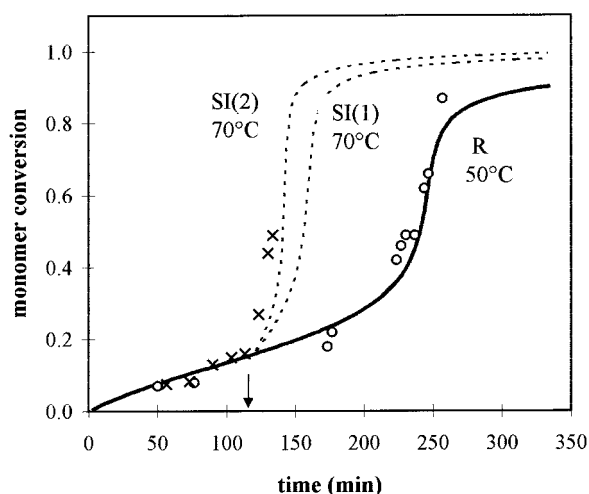

Figure 13 Comparison between model prediction (—, --) and experimental data [(△) 70°C; SD2, (×) 50°C] concerning monomer conversion for a step decrease of temperature (SD2, from 70 to 50°C) during the gel effect; code (b) in Table III; R, reference curve ($T = 70°C$, $I_0 = 0.0258$ mol/L).

m

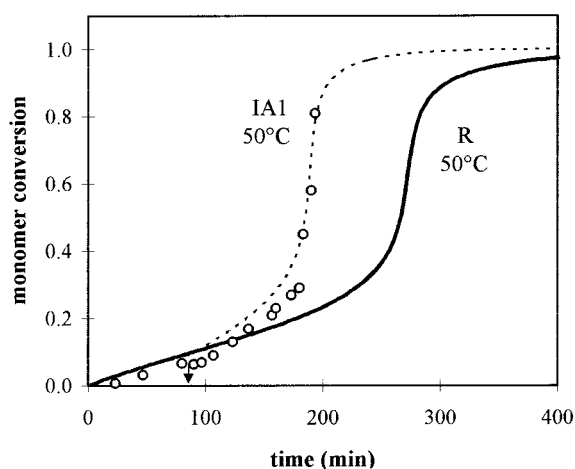3e

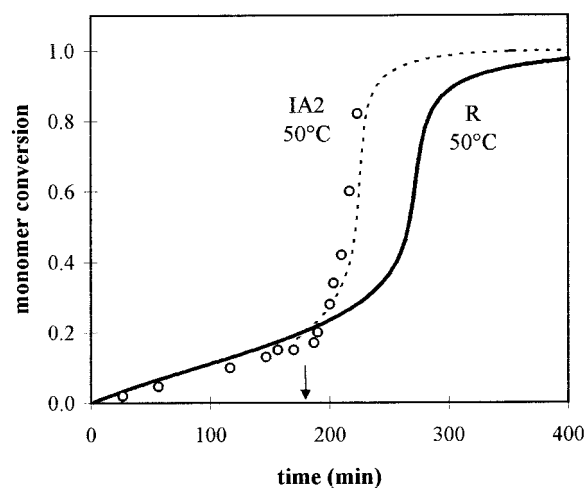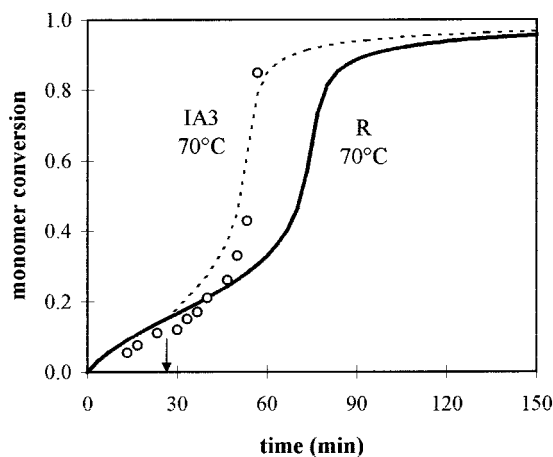

Figure 18 Comparison between (—, --) the simulated conversion and (○) experimental data for the intermediate addition of initiator (IA3, from 0.01548 to 0.1 mol/L) before the gel effect at 70°C; code (f) in Table III.

2. The addition of the initiator before the gel effect results in a decrease of the molecular weight and an early occurrence of the effect. Performing this operation between gel or glass effects produces no changes in conversion or molecular weight.
3. The intermediate addition of the monomer amount before or during the gel effect determines a delay in the settling of the gel effect occurrence and an increase of the molecular weight.

The article represents a first approach corresponding to nonisothermal operation conditions where an approximation is made: the instantaneous change of temperature. This is a limitation of the model. Subsequently, other investigations are in progress to improve the nonisothermal mathematical model. A transition period should be analyzed where a dT/dt term must be considered in the model. However, in this stage of the study the qualitative information was obtained for step changes of the temperature.

In conclusion, because these intermediate operations influence the molecular weights and the time at which the gel effect appears, they can be used to obtain a polymer with desirable properties.

One should emphasize that this model is proposed and tested for applicability in complex engineering studies of polymerization reactions.

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