Solution of Free Radical Polymerization

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SYNOPSIS

The steady state approximation in free radical polymerization is known to break down during the operation of commercial reactors, in which case the unsteady mole balance of polymer radicals have to be solved numerically. We observed that the differential equations governing the zeroth, first, and second moments of polymer radicals in free radical polymerization are nonlinear in nature. The numerical solution of these is "stiff" because the concentration of polymer radicals is very small. Assuming an isothermal reactor, in the absence of the gel effect, these differential equations can be transformed in a suitable new domain where they are linear and can be solved analytically. We have subsequently developed a computer program for nonisothermal reactors in the presence of the gel effect using the analytical solution between any time increment. The results have been compared with those obtained from the fourth order Runge–Kutta technique. We show that when the temperature changes are fast, the Runge–Kutta technique cannot handle the stiffness, and the results begin to deviate from the exact solution. We find that our computer program is computationally efficient in handling this stiffness, takes considerably less time, and can be adapted to any personal computer.

INTRODUCTION

The chain growth polymerization has been studied by several researchers and has been confirmed to consist of the following three reaction steps.[1-5]

Initiation:

$$I_2 \xrightarrow{k_d} 2I$$

$$I + M \xrightarrow{k_1} P_1^\bullet$$

Propagation:

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

Termination and Transfer:

$$P_n^\bullet + I \xrightarrow{k_{tP}} M_n$$

$$P_n^\bullet + P_m^\bullet \xrightarrow{k_{tc}} M_{n+m}$$

$$P_n^\bullet + P_m^\bullet \xrightarrow{k_{td}} M_n + M_m$$

$$P_n^\bullet + S \xrightarrow{k_{tr}} M_n + P_1 \qquad (1)$$

In order to simplify the analysis in the chain growth polymerization, the equal reactivity hypothesis is assumed to be valid. According to this hypothesis, all molecular species react with rate constants that are independent of chain length.

It has been found experimentally that all primary radicals, I, do not lead to propagation due to waste side reactions. In the literature, initiator efficiency f is defined, which represents the fraction of primary radicals utilized in chain growth. There are several factors that affect the initiator efficiency and these have been discussed in the literature in detail.[6-12]

After a certain conversion (around 10%), the well-known gel effect, which corresponds to a large acceleration in the rate of polymerization, and an associated increase in the molecular weight set in. Numerous theoretical and experimental studies of the gel effect have been reported and it is generally agreed that the effect is due to the reduction in the termination rate constants, k_{tc} and k_{td}.[13-24] Near the final polymerization (for conversions greater than 70–80%), when the reaction mass becomes highly viscous, the chain propagation becomes diffusion controlled. As a result of the reduction in k_p, the rate of polymerization takes a dip, which ultimately

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goes to zero as the reaction temperature becomes the same as the glass transition temperature of the polymerizing mixture. This behavior is known as the glass effect.[25-28]

Most of the studies of chain growth polymerization in reactors assume isothermal reactor operation. In commercial practice, however, reactors cannot be maintained in isothermal conditions. Practical problems of heat transfer and thermal runaway invariably occur.[29-47] Because of their simplicity and low cost, tubular reactors are commercially employed and, in the literature, they have been theoretically as well as experimentally investigated.[35-42] The control of molecular weight distribution (MWD) has been carried out by programmed monomer and solvent addition and these have been studied in the literature.[44-46]

In earlier studies of free radical polymerization, it was commonly assumed that the quasi steady state approximation (QSSA) holds. Under this approximation, the rate of formation and the rate of depletion of the polymer radicals are equal. Therefore,

$$k_t[P]_s^2 = 2fk_d[I_2] \tag{2}$$

Here $[P]_s$ represents the total concentration of polymer radicals with QSSA valid and $[I_2]$ is the initiator concentration. However, when gel effect sets in, k_t has been shown to decrease in value, which will result in increased $[P]_s$ under QSSA, and which will lead to higher rates of polymerization. Since all polymerization reactions are exothermic in nature, the temperature of the polymer mass would increase for the same cooling rate, which, in turn, would give a higher rate of initiation. Hence, under the influence of gel effect, the upward thermal drift always occurs and the QSSA breaks down.

If the QSSA breaks down, the mole balance relation for polymer radicals $[P]$ would be governed by a nonlinear first order differential equation instead of by the simple relation given in eq. (2). The concentration $[P]$ in the reaction mass is normally a very small number compared with the monomer or initiator concentration. As an example, styrene polymerized at 60°C with benzoyl peroxide initiator, $[P]_s$ [as calculated from eq. (2)], is of the order 10^{-8} moles per liter. As a consequence, in the numerical computation of $[P]$ through its governing differential equation, the time increment chosen (Δt) must be very small. This means that the differential equations governing the performance of the tubular reactor carrying out radical polymerization are numerically extremely "stiff" and the numerical solution is computationally time consuming.

In this work, we have recorded the transient mole balance relation for all species in the reaction mass. Assuming that the various rate constants for the mechanism of isothermal free radical polymerization given in eq. (1) are time independent, we develop the complete analytical solution. We have also integrated the energy balance equation making use of the above assumption. After every time step, Δt, we estimate the temperature; rate constants are evaluated at the new temperature, which are used in calculating $[M]$, $[P]$, and other quantities in the next time step. This removes the stiffness of the differential equation and the results are obtained conveniently in negligibly small computation time.

THEORETICAL DEVELOPMENTS

It is possible to make mole balance for various species in the reaction mass. The batch reactor results are given in Table I. We define the concentration of polymer radicals, $[P]$, as:

$$[P] = \sum_{n=1}^{\infty} [P_n] \tag{3}$$

With the help of eq. (1.2) of Table I, one can derive an expression for the time variation of $[P]$ as below:

$$\frac{d[P]}{dt} = 2fk_d[I_2] - k_t[P]^2 \tag{4}$$

When the gel and thermal effects are present in radical polymerization, the rate constants k_d and k_t are dependent on temperature and monomer conversion and therefore cannot be integrated. We will show that eq. (4) has a solution for constant k_d and k_t and then develop an analytical solution for isothermal polymerization in the absence of the gel effect. Subsequently, we will show that these results can be naturally adopted in the presence of the gel and thermal effects.

Solution of Isothermal Radical Polymerization

The mole balance for the initiator given in eq. (1.1) of Table I can be integrated for time invariant fk_d as

$$[I_2] = [I_2]_0 e^{-k_d t} \tag{5}$$

Table I Mole and Energy Balance Relation for Various Species in Batch (or Tubular) Reactors Carrying out Radical Polymerization

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(A) Distribution Balance:

1. Initiator, I_2

$$\frac{d[\mathbf{I}_2]}{dt} = - k_d[I_2] \tag{1.1}$$

2. Growing Polymer Radicals, $[P_n]$, of chain length n ($n = 1, 2, 3 \ldots$)

$$[P] = \sum_{n=1}^{\infty} [P_n]$$

$$\frac{d[P_1]}{dt} = k_I[I][M] - k_p[P_1][M] - k_t[P_1][P] + k_{tr}[S]\{[P] - [P_1]\}$$

$$\frac{d[P_n]}{dt} = k_p[M][[P_{n-1}] - [P_n]] - k_t[P_n][P] - k_{tr}[S][P_n] \tag{1.2}$$

3. Monomer, M

$$\frac{d[M]}{dt} = - k_p[P][M] \tag{1.3}$$

4. Inactive Polymer, $[M_n]$, of chain length n ($n = 2, 3, \ldots$)

$$\frac{d[M_n]}{dt} = \frac{k_{tc}}{2}\sum_{m=1}^{n-1} [P_m][P_{n-m}] + k_{td}[P_n]\sum_{n=1}^{\infty} [P_n] + k_{tr}[S][P_n] \tag{1.4}$$

5. Energy Balance

$$\rho C_p \frac{dT}{dt} - (-\Delta H_r)k_p[M][P] - \frac{4U}{D}(T-T_w) \tag{1.5}$$

(B) Balance of Moments:

1. $$\frac{d[P]}{dt} = 2fk_d[I_2] - k_t[P]^2 \tag{1.6}$$

2. $$\frac{d[M]}{dt} = k_p[P][M] \tag{1.7}$$

3. $$\frac{d\lambda_0}{dt} = (0.5k_{tc} + k_{td})[P]^2 + k_{tr}[S][P] \tag{1.8}$$

4. $$\frac{dQ_1}{dt} = 2fk_d[I_2] - k_t[P]Q_1 - k_p[M][P] \tag{1.9}$$

5. $$\frac{d\lambda_1}{dt} = (k_{tc} + k_{td})[P]Q_1 + k_{tr}[S]Q_1 \tag{1.10}$$

6. $$\frac{dQ_2}{dt} = 2fk_d[I_2] + k_p[M](2Q_1 + [P]) - k_t[P]Q_2 \tag{1.11}$$

7. $$\frac{d\lambda_2}{dt} = (k_{tc} + k_{td})[P]Q_2 + k_{tc}Q_1^2 + k_{tr}[S]Q_2 \tag{1.12}$$

8. $$\frac{dT}{dt} = \frac{(-\Delta H_r)k_p[M][P]}{\rho C_p} - \frac{4U}{D\rho C_p}(T-T)_w \tag{1.13}$$

In the above equation, $[I_2]_0$ is the concentration of initiator at $t = 0$. Let us now transform $[P]$ in eq. (4)

$$[P] = \frac{1}{k_t}\frac{dy/dt}{y} \qquad (6)$$

and upon substituting eq. (5) for $[I_2]$ in eq. (4), one obtains,

$$\frac{d^2y}{dt^2} = 2fk_dk_t[I_2]_0e^{-k_dt}y \qquad (7)$$

Further, we define x related to time of polymerization as

$$x = 2fk_dk_t[I_2]_0e^{-k_dt} \qquad (8)$$

This gives

$$\begin{aligned} \frac{dx}{dt} &= -k_d\,x && \text{(a)} \\ \frac{dy}{dt} &= \frac{dy}{dx}\frac{dx}{dt} = -k_dx\frac{dy}{dx} && \text{(b)} \\ \frac{d^2y}{dt^2} &= \frac{d}{dx}\left(\frac{dy}{dt}\right)\frac{dx}{dt} && \text{(c)} \\ &= (k_d)^2x\frac{dy}{dx} + (k_d)^2x^2\frac{d^2y}{dx^2} && \text{(d)} \quad (9) \end{aligned}$$

In terms of these, eq. (7) becomes

$$(k_d)^2x^2\frac{d^2y}{dx^2} + (k_d)^2x\frac{dy}{dx} - xy = 0 \qquad (10)$$

we further transform x by

$$Z = 2\sqrt{bx} \qquad \text{(a)}$$

where

$$b = \left(\frac{1}{k_d}\right)^2 \qquad \text{(b)} \quad (11)$$

in terms of which, eq. (10) reduces to

$$Z^2\frac{d^2y}{dZ^2} + Z\frac{dy}{dZ} - (Z^2 - 0)y = 0 \qquad (12)$$

For this, y has the following solution

$$y = C_1I_0(Z) + C_2K_0(Z) \qquad (13)$$

Where $I_0(Z)$ and $K_0(Z)$ are the modified zeroth order Bessel functions and C_1 and C_2 are the constants of integration. With the help of eq. (6), one can derive $[P]$ as

$$\begin{aligned} [P] &= -\frac{k_dZ}{2k_t}\frac{1}{y}\frac{dy}{dZ} && (14) \\ &= \frac{k_dZ}{2k_t}\frac{C_2K_1(Z) - C_1I_1(Z)}{C_2K_0(Z) + C_1I_0(Z)} \\ &= \frac{k_dZ}{2k_t}\frac{K_1(Z) - CI_1(Z)}{K_0(Z) + CI_0(Z)} && (15) \end{aligned}$$

where $C = C_1/C_2$, which is to be determined by the initial conditions.

Let us assume that at $t = 0$, the concentration of Polymer radicals is $[P]_0$. In the Z plane, time $t = 0$ corresponds to Z_0 given by

$$Z_0 = 2\sqrt{\frac{2fk[I_2]_0}{k_d}} \qquad (16)$$

and C in eq. (15) is given by

$$\begin{aligned} C &= \frac{K_1(Z_0) - \dfrac{k_t[P]_0}{k_dZ_0}K_0(Z_0)}{I_1(Z_0) + \dfrac{k_t[P]_0}{k_dZ_0}I_0(Z_0)} \\ &= \frac{\dfrac{K_1(Z_0)}{I_1(Z_0)} - [P]_0^*\dfrac{K_0(Z_0)}{I_1(Z_0)}}{1 + [P]_0^*\dfrac{I_0(Z_0)}{I_1(Z_0)}} && (17) \end{aligned}$$

where

$$[P]_0^* = \frac{[P]_0}{[P]_S} = [P]_0\sqrt{\frac{k_t}{2fk_d[I_2]_0}} \qquad (18)$$

In the above equation, $[P]_s$ is the concentration of polymer radicals, assuming the steady state approximation, and is given by eq. (2).

The variation in the monomer concentration, $[M]$, is governed by eq. (1.3) of Table I. We substitute eq. (11) in the equation to obtain:

$$\frac{d[M]}{dt} = \frac{d[M]}{dZ}\frac{dZ}{dt} = -\frac{k_dZ}{2}\frac{d[M]}{dZ} = -k_p[M][P]$$

or

$$\frac{k_dZ}{2}\frac{d[M]}{dZ} = k_p[M]\frac{fk_dZ}{2k_t}\frac{K_1(Z) - CI_1(Z)}{K_0(Z) + CI_0(Z)}$$

$$\frac{d[M]}{dZ} = [M]\frac{k_p}{k_t}\left(\frac{K_1(Z) - CI_1(Z)}{K_0(Z) + CI_0(Z)}\right) \qquad (19)$$

We substitute

$$u = K_0(Z) + CI_0(Z) \tag{20}$$

which, upon differentiation with respect to Z, gives

$$\frac{du}{dZ} = -K_1(Z) + CI_1(Z) \tag{21}$$

Comparison of eqs. (18) and (20) yields

$$\frac{-d[M]}{[M]} = \frac{k_p}{k_t}\frac{du}{u} \tag{22}$$

which, upon integration, leads to

$$[M] = [M]_0\left[\frac{K_0(Z) + CI_0(Z)}{K_0(Z_0) + CI_0(Z_0)}\right]^{k_p/k_t} \tag{23}$$

In the above equation, $[M]_0$ is the monomer concentration at $t = 0$ (or $Z = Z_0$) and Z_0 is defined in eq. (16).

The magnitude of Z, as defined in eq. (11), is very large. For example, for methyl methacrylate polymerizing at 60°C with AIBN $[I_2]_0 = 0.0258$ mol/L] initiator, the rate constants k_d, k_p, and k_t are $0.475 \times 10^{-3}\ \text{min}^{-1}$, 0.4117×10^5 L/mol min, and 0.20383×10^{10} L/mol min, respectively. Taking initiator efficiency f to be 0.58, we get at time $t = 0$ that "b", as defined in eq. (11), and x_0, as defined by eq. (8), to be 1.3175×10^7 and 2.8756×10^4, respectively. Therefore, Z at time $t = 0$ is given in eq. (16) and is equal to 0.1231×10^7. Hence, the asymptotic expansion of Bessel functions valid for large arguments ($Z > 5$) may be used.[49] When we later consider the time dependent polymerization, due to changing temperature rate constants and properties of the reaction mass, conditions could arise when this approximation may not be valid. However, for most isothermal polymerizations, the asymptotic expansion is valid and is not limited to the MMA system only.

Neglecting terms involving Z in the denominator, we get

$$K_1(Z) = K_0(Z) = \sqrt{\frac{\pi}{2Z}}\, e^{-Z}$$

$$I_1(Z) = I_0(Z) = \frac{e^Z}{\sqrt{2\pi Z}} \tag{24}$$

Making use of the above approximations for Bessel functions, C defined in eq. (17) yields

$$C = \psi\pi e^{-2Z_0} \quad \text{where} \quad \psi = \frac{1 - [P]_0^*}{1 + [P]_0^*} \tag{25}$$

The eq. (16), for $[P]$, may be written as

$$[P] = \frac{k_d Z}{2k_t} - \frac{\dfrac{K_1(Z)}{I_0(Z)} - C\dfrac{I_1(Z)}{I_0(Z)}}{\dfrac{K_0(Z)}{I_0(Z)} + C}$$

After substituting for C and Bessel functions, we get an expression for the time variation of $[P]$ as

$$[P] = \frac{k_d Z}{2k_t} - \frac{1 - \psi e^{-2(Z_0-Z)}}{1 + \psi e^{-2(Z_0-Z)}} \tag{26}$$

The quantities $CI_0(Z)$ and $CI_0(Z_0)$ in eq. (23), for $[M]$ are given by

$$CI_0(Z) = \psi\pi e^{-Z_0}\frac{e^{-(Z_0-Z)}}{\sqrt{2\pi Z}}$$

$$CI_0(Z_0) = \frac{\psi\pi e^{-Z_0}}{\sqrt{2\pi Z_0}} \tag{27}$$

These may be taken as zero, since both Z_0 and Z are of the order 10^6. Hence eq. (23) for $[M]$ simplifies to

$$[M] = [M]_0 e^{-m(Z_0-Z)} \tag{28}$$

where

$$m = \frac{k_p}{k_t}$$

The balance for the transfer agent S is given by

$$\frac{d[S]}{dt} = -k_{tr}[S][P] \tag{29}$$

Dividing this by eq. (1.3) of Table I for the balance of monomer, one has

$$\frac{d[S]}{[S]} = \frac{k_{tr}}{k_p}\frac{d[M]}{[M]} \tag{30}$$

which upon integration, yields

$$\frac{[S]}{[S]_0} = \left\{\frac{[M]}{[M]_0}\right\}^{k_{tr}/k_p} \tag{31}$$

In the above equation, $[S]_0$ is the initial concentration of the transfer agent.

By making use of the above expressions for $[M]$, $[S]$, and $[P]$, we can obtain analytical expressions for various moments of radical and dead polymer distributions as follows.

Radical and Dead Polymer Moments

The differential equation for first moment Q_1 for radical distribution $(= \sum_{n=1}^{\infty} n[p_n])$ can be derived from eq. (1.2) of Table I as follows

$$\begin{aligned}\frac{dQ_1}{dt} &= -k_t[P]Q_1 + 2fk_d[I_2] + k_p[M]\{2[P_1] \\ &\quad + 3[P_2] + 4[P_3] + \cdots\} - K_p[M] \\ &\quad \times \{[P_1] + 2[P_2] + \cdots\} \\ &= -k_t[P]Q_1 + 2fk_d[I_2] + k_p[M] \\ &\quad \times \{(1[P_1] + 2[P_2] + 3[P_3] + \cdots) \\ &\quad + ([P_1] + [P_2] + [P_3] + \cdots)\} \\ &\quad - k_p[M]\{[P_1] + 2[P_2] + 3[P_3]\cdots\}\end{aligned}$$

$$\frac{dQ_1}{dt} = 2fk_d[I_2] - k_t[P]Q_1 + k_p[M][P] \qquad (32)$$

The above equation is a linear differential equation of the first order, if we assume rate constants as time invariant. We get the integrating factor $(I.F.)$ as follows

$$I.F = \exp\left\{k_t \int [P]dt\right\} \qquad (33)$$

Observing that

$$\frac{d\{[M]/[M]_0\}}{\{[M]/[M]_0\}} = -k_p[P]dt \qquad (34)$$

eq. (33) reduces to

$$\begin{aligned}I.F &= \exp\left\{-\frac{1}{m}\, ln\left(\frac{[M]}{[M]_0}\right)\right\} \\ &= \left\{\frac{[M]}{[M]_0}\right\}^{-1/m}\end{aligned} \qquad (35)$$

The integration of the differential equation (eq. 32) gives Q_1 as

$$\begin{aligned}Q_1\left\{\frac{[M]}{[M]_0}\right\}^{-1/m} &= \int \left(2fk_d[I_2] + k_p[M]_0\left\{\frac{[M]}{[M]_0}\right\}[P]\right) \\ &\quad \times \left\{\frac{[M]}{[M]_0}\right\}^{-1/m} dt\end{aligned}$$

Substituting $[I_2]$ from eq. (11) in terms of Z as

$$[I_2] = \frac{Z^2 k_d}{8fk_t}$$

and carrying out the integration to finally obtain,

$$Q_1 = C_1\left(\frac{[M]}{[M]_0}\right) + C_2\left(\frac{[M]}{[M]_0}\right)^{1/m} + \frac{k_d}{2k_t}(Z+1) \qquad (36)$$

where

$$C_1 = \frac{-[M]_0}{1 - 1/m} \quad \text{and}$$

$$C_2 = Q_{10} + \frac{[M]_0}{1 - 1/m} - \frac{k_d}{2k_t}(Z_0 + 1) \qquad (37)$$

In order to derive the differential equations governing zeroth, first, and second moments of dead polymer distribution, we make use of the mole balance for M_n from Table I. We have

$$\begin{aligned}\frac{d[M_n]}{dt} &= \frac{k_{tc}}{2}\sum_{m=1}^{n-1}[P_m][P_{n-m}] \\ &\quad + k_{td}[P_n]\sum_{n=1}^{\infty}[P_n] + k_{tr}[S]\sum_{n=1}^{\infty}[P_n]\end{aligned} \qquad (38)$$

Furthermore, we know that,

$$\begin{aligned}&\sum_{n=2}^{\infty} n^k \sum_{m=1}^{n-1}[P_m][P_{n-m}] \\ &\quad = \sum_{n=1}^{\infty}[P_n]\sum_{m=1}^{n-1}(m+n)^k[P_m]\end{aligned} \qquad (39)$$

The zeroth moment of dead polymer distribution $\lambda_0 = (\sum_n M_n)$ can be derived by adding eq. (38) for all n

$$\frac{d\lambda_0}{dt} = \frac{k_{tc}}{2}[P]^2 + k_{td}[P]^2 + k_{tr}[S][P] \qquad (40)$$

where $[P] = \sum_{n=1}^{\infty} [P_n]$ and, making use of eq. (34),

$$[P]dt = \frac{-1}{k_p} \frac{d\{[M]/[M]_0\}}{\{[M]/[M]_0\}}$$

we get,

$$\int d\lambda_0 = \frac{-(0.5k_{tc} + k_{td})}{k_p} \int [P] \frac{d\{[M]/[M]_0\}}{\{[M]/[M]_0\}} + \int k_{tr}[S][P]dt$$

From eq. (28),

$$\frac{d\{[M]/[M]_0\}}{\{[M]/[M]_0\}} = mdZ$$

and hence

$$\lambda_0 - \lambda_{00} = -\frac{(0.5k_{tc} + k_{td})m}{k_P} \int [P]dZ + \int k_{tr}[S][P]dt \quad (41)$$

Substituting for $[P]$ from eq. (27), we get

$$\lambda_0 - \lambda_{00} = \int d\lambda_0 = -(0.5k_{tc} + k_{td}) \frac{m}{k_p} \frac{k_d}{2k_t} \int Z \times \frac{1 - \psi e^{-2(Z_0 - Z)}}{1 + \psi e^{-2(Z_0 - Z)}} dz + ([S] - [S]_0) + \text{const.} \quad (42)$$

The rigorous evaluation of the integral leads to an infinite series and is given in Appendix I. However, if Z above is assumed to be approximately equal to Z_0, the integration in eq. (42) is considerably simplified without much affecting the results. Thus, eq. (42) leads to

$$\lambda_0 - \lambda_{00} = \int d\lambda_0 = -(0.5k_{tc} + k_{td}) \frac{m}{k_p} \frac{k_d Z_0}{2k_t} \times \int \frac{1 - \psi e^{-2(Z_0 - Z)}}{1 + \psi e^{-2(Z_0 - Z)}} dZ + ([S] - [S]_0) \quad (43)$$

This can be easily integrated to

$$\lambda_0 - \lambda_{00} = \frac{(0.5k_{tc} + k_{td})}{4k_p k_t} mk_d Z_0 \Big[2(Z_0 - Z) - 2\,ln(1 + \psi) + 2\,ln(1 + \psi e^{-2(Z_0 - Z)}) \Big] + ([S] - [S]_0) \quad (44)$$

The differential equation for first moment $\left(\lambda_1 = \sum_{n=1}^{\infty} n[M]_n\right)$ of dead polymer distribution is similarly derived using eqs. (38) and (39) as follows:

$$\begin{aligned} \frac{d\Sigma n[M_n]}{dt} &= k_{td}[P] \sum_{n=0}^{\infty} n[P_n] + \frac{k_{tc}}{2} \sum_{n=0}^{\infty} [P_n] \sum_{m=1}^{n-1} (m + n)[P_m] \\ &= k_{td}[P]Q_1 + \frac{k_{tc}}{2} \sum_{n=0}^{\infty} [P_n](Q_1 + n[P]) \\ &= k_{td}[P]Q_1 + \frac{k_{tc}}{2} 2Q_1[P] \end{aligned} \quad (45)$$

Upon elimination of $[P]$, with the help of eq. (1.3) of Table I,

$$\frac{d\lambda_1}{dt} = -\frac{k_t}{k_p} \frac{Q_1}{\{[M]/[M_0]\}} \frac{d\{[M]/[M_0]\}}{dt} + k_{tr}[S]Q_1$$

Substituting for Q_1, and using

$$\frac{d\{[M]/[M]_0\}}{\{[M]/[M]_0\}} = mdZ$$

we get,

$$\begin{aligned} \lambda_1 - \lambda_{10} = &-\frac{k_t}{k_p} \left[\int_1^{[M]/[M]_0} \left(C_1 + C_2 \left(\frac{[M]}{[M]_0} \right)^{(\frac{1}{m} - 1)} \right. \right. \\ &\left. \times d\left(\frac{[M]}{[M]_0} \right) + \int_{Z_0}^{Z} \frac{k_d}{2k_t} (Z + 1)\, mdZ \right] \\ &+ \int k_{tr} C_1 [S]_0 e^{p_1 (Z_0 - Z)} dt \\ &+ \int k_{tr} C_2 [S]_0 e^{p_2 (Z_0 - Z)} dt \\ &+ \int k_{tr} \frac{k_d (Z + 1)}{2k_t} [S]_0 e^{(p_2 + 1)(Z_0 - Z)} dt \end{aligned}$$

where λ_{10} is the value of λ_1 at time $t = 0$ and C_1 and C_2 are as defined in eq. (37).

Upon integration, we obtain,

$$\lambda_1 - \lambda_{10} = \frac{k_t}{k_p} \left[C_1 \left(1 - \frac{[M]}{[M]_0} \right) + mC_2 \left(1 - \left(\frac{[M]}{[M]_0} \right)^{1/m} \right) \right]$$

$$+\frac{k_d}{2k_t}\left[\frac{1}{2}(Z_0^2 - Z^2) + (Z_0 - Z)\right]$$

$$+\frac{2k_{tr}C_1[S]_0}{k_dZ_0p_1}(e^{p_1(Z_0-Z)} - 1) + \frac{2k_{tr}C_2[S]_0}{k_dZ_0p_2}$$

$$\times (e^{p_2(Z_0-Z)} - 1) + \frac{2k_{tr}[S]_0}{p_3k_t}(e^{p_3(Z_0-Z)} - 1)$$

$$+\frac{2k_{tr}[S]_0}{p_3Z_0k_t}(e^{p_3(Z_0-Z)} - 1) \quad (46)$$

where $p_1 = -m(n+1), p_2 = -(mn+1), p_3 = -mn$, and $n = k_{tr}/k_p$.

The expression for second moment of polymer radical distribution, Q_2 ($= \sum n^2[P_n]$), is derived making use of eq. (1.2) of Table I, to obtain

$$\frac{dQ_2}{dt} = -k_t[P]Q_2 + 2fk_d[I_2] + k_p[M]$$

$$\times (2^2[P_1] + 3^2[P_2] + 4^2[P_3] + \cdots)$$

$$- k_pM([P_1] + 2^2[P_2] + 3^2[P_3] + \cdots)$$

$$= -k_t[P]Q_2 + 2fk_d[I_2] + k_p[M]$$

$$\times (1^2[P_1] + 2^2[P_2] + 3^2[P_3] + \cdots)$$

$$+ ([P_1] + [P_2] + [P_3] + \cdots) + (2.1[P_1]$$

$$+ 2.2[P_2] + \cdots) - K_p[M]Q_2$$

$$= -k_t[P]Q_2 + 2fk_d[I_2]$$

$$+ k_p[M](2Q_1 + [P]) \quad (47)$$

This is again a linear differential equation of first order. As before, the integrating factor is equal to $\left(\frac{[M]}{[M]_0}\right)^{-1/m}$, and hence

$$Q_2\left(\frac{[M]}{[M]_0}\right)^{-1/m} = \int \left(\frac{[M]}{[M]_0}\right)^{-1/m}\left[2fk_d[I_2] + 2k_p\right.$$

$$\left.\times [M_0]\left(\frac{[M]}{[M]_0}\right)Q_1 + b_p[M_0][P]\right]dt + \text{constant}$$

Substituting for $[I_2]$ and Q_1, we get

$$Q_2\left(\frac{[M]}{[M]_0}\right)^{-1/m} = \int 2fk_d\frac{Z^2k_d}{8k_tf}e^{(Z_0-Z)} - \frac{2\,dZ}{-k_dZ}$$

$$+ \int 2k_p[M_0]\left(\frac{[M]}{[M]_0}\right)^{-1/m}$$

$$\times \left[C_1\left(\frac{[M]}{[M]_0}\right) + C_2\left(\frac{[M]}{[M]_0}\right)^{1/m} + \frac{k_d}{2k_t}(Z+1)\right] \times \frac{2\,dZ}{-k_dZ}$$

$$+ \int \left(\frac{[M]}{[M]_0}\right)^{-1/m} d\left(\frac{[M]}{[M]_0}\right) + C^* \quad (48)$$

We integrate the above expression assuming $Z = Z_0$. The rigorous solution has also been derived and is presented in Appendix I. We find that the results derived in the following equation yields results that are accurate to within 0.01%.

$$Q_2 = \frac{k_d(Z+1)}{2k_t} - \frac{4k_p[M]_0C_1}{k_dZ_0(2m-1)}\left(\frac{[M]}{[M]_0}\right)^2$$

$$- \frac{4k_p[M]_0C_2}{k_dZ_0m}\left(\frac{[M]}{[M]_0}\right)^{1+1/m} - \frac{2k_p[M]_0}{k_t(m-1)}$$

$$\times \left(\frac{[M]}{[M]_0}\right) - \frac{2k_p[M]_0}{k_tZ_0(m-1)}\left(\frac{[M]}{[M]_0}\right)$$

$$- \frac{[M]_0}{1-1/m}\left(\frac{[M]}{[M]_0}\right) + C^*\left(\frac{[M]}{[M]_0}\right)^{1/m} \quad (49)$$

where C^* is evaluated using the initial condition $Q_2 = Q_{20}$ at $t = 0$. Therefore we get

$$C^* = Q_{20} - \frac{fk_d(Z_0+1)}{2k_t} + \frac{4k_p[M]_0C_1}{k_dZ_0(2m-1)}$$

$$+ \frac{4k_p[M]_0C_2}{k_dZ_0m} + \frac{2k_p[M]_0}{k_t(m-1)}$$

$$+ \frac{2k_p[M]_0}{k_tZ_0(m-1)} + \frac{[M]_0}{1-1/m} \quad (50)$$

The differential equation for second moment, $\lambda_2 = \sum n^2[M_n]$, of dead polymer distribution is derived using the Mole balance relation (eq. 38) and eq. (39) as follows:

$$\frac{d\lambda_2}{dt} = k_{td}[P]Q_2 + \frac{k_{tc}}{2}\sum n^2 \sum [P_n][P_{m-n}]$$

$$+ k_{tr}[S]\sum n^2[P_n]$$

$$= k_{td}[P]Q_2 + \frac{k_{tc}}{2}\sum [P_n]$$

$$\times \sum (m^2 + n^2 + 2nm)[P_n] + k_{tr}[S]Q_2$$

$$= k_{td}[P]Q_2 + \frac{k_{tc}}{2}([P]Q_2 + [P]Q_2 + 2Q_1^2)$$

$$+ k_{tr}[S]Q_2$$

$$= (k_{tc} + k_{td})[P]Q_2 + k_{tc}Q_1^2 + k_{tr}[S]Q_2 \quad (51)$$

We observe that

$$
\begin{aligned}
\int k_{tc} Q_1^2 dt = \frac{-2k_{tc}}{k_d} \int \Bigg[& C_1^2 \left(\frac{[M]}{[M]_0}\right)^2 \\
& + C_2^2 \left(\frac{[M]}{[M]_0}\right)^{2/m} + \left(\frac{k_d}{2k_t}\right)^2 (Z^2 + 2Z + 1) \\
& + 2C_1C_2 \left(\frac{[M]}{[M]_0}\right)^{1+1/m} + C_1 \left(\frac{k_d}{k_t}\right)\left(\frac{[M]}{[M]_0}\right)(Z + 1) \\
& + C_2 \left(\frac{k_d}{k_t}\right)(Z + 1)\left(\frac{[M]}{[M]_0}\right)^{1/m} \Bigg] \frac{dz}{Z}
\end{aligned}
\tag{52}
$$

Integrating the above equation, assuming $Z = Z_0$ in the denominator and taking it out of the integral, we get

$$
\begin{aligned}
\int k_{tc} Q_1^2 dt = \frac{2k_{tc}}{k_d} \Bigg[& \frac{C_1^2}{2mZ_0} \left(1 - \left(\frac{[M]}{[M]_0}\right)^2\right) \\
& + \frac{C_2^2}{2Z_0} \left(1 - \left(\frac{[M]}{[M]_0}\right)^{2/m}\right) \\
& + \left(\frac{k_d}{2k_t}\right)^2 \left[\frac{1}{2}(Z_0^2 - Z^2) + 2(Z_0 - Z) + ln\left(\frac{Z_0}{Z}\right)\right] \\
& + \frac{2C_1C_2}{(m+1)Z_0} \left(1 - \left(\frac{[M]}{[M]_0}\right)^{1+1/m}\right) + \frac{C_1}{m}\frac{k_d}{k_t} \\
& \times \left(1 - \left(\frac{[M]}{[M]_0}\right)\right) + \frac{C_1}{mZ_0}\left(\frac{k_d}{k_t}\right)\left(1 - \left(\frac{[M]}{[M]_0}\right)\right) \\
& + \frac{C_2 k_d}{k_t} \left(1 - \left(\frac{[M]}{[M]_0}\right)^{1/m}\right) \\
& + \frac{C_2 k_d}{k_t Z_0} \left(1 - \left(\frac{[M]}{[M]_0}\right)^{1/m}\right) \Bigg]
\end{aligned}
\tag{53}
$$

Also,

$$
\int k_t [P] Q_2 dt = \frac{-k_t}{k_p} \int \frac{Q_2}{\left(\frac{[M]}{[M]_0}\right)} d\left(\frac{[M]}{[M]_0}\right)
$$

Substituting Q_2 from eq. (50), and carrying out the integration assuming $Z = Z_0$ is in the denominator, we get

$$
\begin{aligned}
& \int k_t [P] Q_2 dt \\
& = \frac{k_t}{k_p} \Bigg[\frac{mk_d}{2k_t} \left[\frac{1}{2}(Z_0^2 - Z^2) + (Z_0 - Z)\right] \\
& - \frac{2k_p [M]_0 C_1}{k_d Z_0 (2m - 1)} \left(1 - \left(\frac{[M]}{[M]_0}\right)^2\right) \\
& - \frac{4k_p [M]_0 C_2}{k_d Z_0 (m + 1)} \left(1 - \left(\frac{[M]}{[M]_0}\right)^{1+1/m}\right) \\
& - \frac{2k_p [M]_0}{k_t (m - 1)} \left(1 - \left(\frac{[M]}{[M]_0}\right)\right) - \frac{2k_p [M]_0}{k_t Z_0 (m - 1)} \\
& \times \left(1 - \left(\frac{[M]}{[M]_0}\right) - \frac{[M]_0}{1 - \frac{1}{m}} \left(1 - \frac{[M]}{[M]_0}\right)\right. \\
& \qquad + mC^* \left(1 - \left(\frac{[M]}{[M]_0}\right)^{1/m}\right) \Bigg]
\end{aligned}
\tag{54}
$$

where C^* is as defined in eq. (50). Therefore,

$$
\begin{aligned}
\lambda_2 - \lambda_{20} = \frac{2k_{tc}}{k_d} & \left[\frac{C_1^2}{2mZ_0} \left(1 - \left(\frac{[M]}{[M]_0}\right)^2\right) + \frac{C_2^2}{2Z_0} \left(1 - \left(\frac{[M]}{[M]_0}\right)^{2/m}\right) \right. \\
& + \left(\frac{k_d}{2k_t}\right)^2 \left[\frac{1}{2}(Z_0^2 - Z^2) + 2(Z_0 - Z) + ln\left(\frac{Z_0}{Z}\right)\right] + \frac{2C_1C_2}{(m+1)Z_0}\left(1 - \left(\frac{[M]}{[M]_0}\right)^{1+1/m}\right) + \frac{C_1}{m}\frac{k_d}{k_t}\left(1 - \left(\frac{[M]}{[M]_0}\right)\right) \\
& \left. + \frac{C_1}{mZ_0}\left(\frac{k_d}{k_t}\right)\left(1 - \left(\frac{[M]}{[M]_0}\right)\right) + \frac{C_2 k_d}{k_t}\left(1 - \left(\frac{[M]}{[M]_0}\right)^{1/m}\right) + \frac{C_2 k_d}{k_t Z_0}\left(1 - \left(\frac{[M]}{[M]_0}\right)^{1/m}\right) \right] \\
& + \frac{k_t}{k_p}\left[\frac{mk_d}{2k_t}\left[\frac{1}{2}(Z_0^2 - Z^2) + (Z_0 - Z)\right] - \frac{2k_p [M]_0 C_1}{k_d Z_0 (2m - 1)}\left(1 - \left(\frac{[M]}{[M]_0}\right)^2\right) - \frac{4k_p [M]_0 C_2}{k_d Z_0 (m + 1)}\right. \\
& \times \left(1 - \left(\frac{[M]}{[M]_0}\right)^{1+1/m}\right) - \frac{2k_p [M]_0}{k_t (m - 1)}\left(1 - \left(\frac{M}{M_0}\right)\right) - \frac{2k_p [M]_0}{k_t Z_0 (m - 1)}\left(1 - \left(\frac{[M]}{[M]_0}\right) - \frac{[M]_0}{1 - \frac{1}{m}}\left(1 - \frac{[M]}{[M]_0}\right)\right.
\end{aligned}
$$

$$
\begin{aligned}
&+ mC^*\left(1 - \left(\frac{[M]}{[M]_0}\right)^{1/m}\right)\Bigg] + \frac{k_{tr}[S]_0}{p_3 k_t}\left(e^{p_3(Z_0-Z)} - 1\right) + \frac{k_{tr}[S]_0}{p_3 Z_0 k_t}\left(e^{p_3(Z_0-Z)} - 1\right) \\
&- \frac{8[S_0]k_p[M]_0C_1}{(k_dZ_0)^2(2m-1)p_4}\left(e^{p_4(Z_0-Z)} - 1\right) - \frac{8[S]_0k_p[M]_0C_2}{(k_dZ_0)^2(2m-1)p_5}\left(e^{p_5(Z_0-Z)} - 1\right) - \frac{4k_p[M]_0[S]_0}{k_tk_dZ_0(m-1)p_1} \\
&\times \left(e^{p_1(Z_0-Z)} - 1\right) - \frac{4k_p[M]_0[S]_0}{k_tk_dZ_0^2(m-1)p_1}\left(e^{p_1(Z_0-Z)} - 1\right) - \frac{2[M]_0[S]_0}{(1-1/m)k_dZ_0p_1}\left(e^{p_1(Z_0-Z)} - 1\right) \\
&\qquad + \frac{2C^*[S]_0}{k_dZ_0p_2}\left(e^{p_2(Z_0-Z)} - 1\right) \qquad (55)
\end{aligned}
$$

$$p_4 = -m(n+2)$$

$$p_5 = -(mn+m+1)$$

COMPUTATIONAL TECHNIQUES

We have derived the analytical solution for isothermal radical polymerization in batch reactors. In order to check the consistency of these results, we have computed the various reactor parameters using the fourth order Runge–Kutta numerical technique and we have checked our results against the analytical solution. The flow chart of the fourth order Runge–Kutta technique is given in Figure 1 and we have varied Δt in Table II and seen its effect upon the numerical solution. For stable solution, we find that the time increment Δt must be about 0.0001 min. The flow chart of computation for our analytical solution is given in Figure 2. It must be observed that our analytical solution are given in terms of the Z variable. For the isothermal reactor, there is a straight forward exponential relation. However, for nonisothermal cases, there is an ambiguity in terms of properly defining Z. This arises because, in general, the rate constants vary with time of polymerization. To overcome this difficulty, we recall that in the Runge–Kutta technique, the total time of polymerization is divided into small incremental time. The concentration parameters, $[M]$, λ_0, λ_1, λ_2, $[P]$, Q_1, and Q_2, for the next incremental time, are calculated using their values at a given time. This fact has been shown in Figure 2. In such computations, the reaction parameters are assumed to be time invariant between the incremental times.

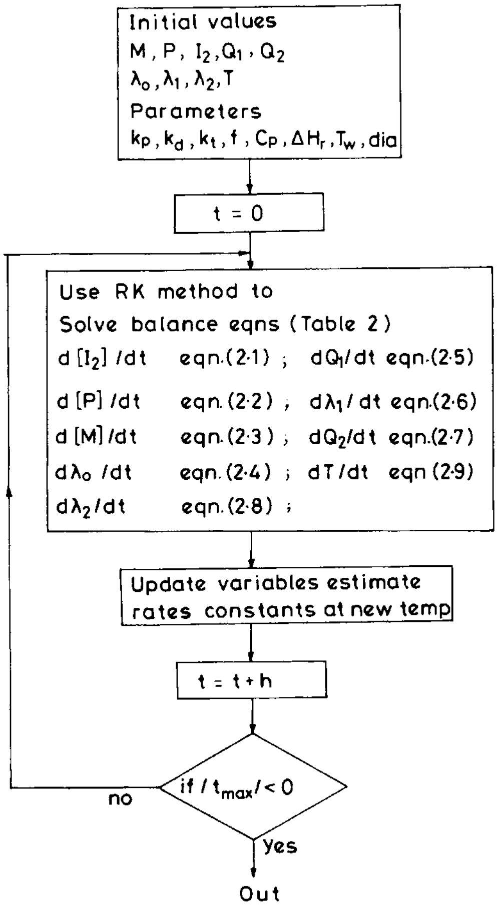

Figure 1 Runge–Kutta scheme for free radical polymerization.

For the cases in which the temperature of polymerization changes as well as gelation occurs, we similarly divide the total time of polymerization into small incremental times. Between these time increments, we assume that the rate constants are time invariant. If we assume this, all the results for isothermal reactors are valid between the incremental time; only the energy balance equation remains to be integrated as shown below.

The modelling of nonisothermal polymerization can be done by inclusion of the following energy balance,

$$\rho C_p \frac{dT}{dt} = (-\Delta H_r)k_p[M][P] - \frac{4U}{D}(T - T_W) \qquad (56)$$

Table II Stable Time Step for Fourth Order Runge Kutta Method

Time (min)	Δt = 0.02 min		Δt = 0.01 min		Δt = 0.005 min		Δt = 0.0001 min	
	$[P]$	λ_0	$[P] \times 10^7$	$\lambda_0 \times 10^4$	$[P] \times 10^7$	$\lambda_0 \times 10^4$	$[P] \times 10^7$	$\lambda_0 \times 10^4$
10	—	—	0.2175	0.1305	0.83503	0.1299	0.83503	0.1299
20	—	—	0.2193	0.2607	0.8349	0.26066	0.8349	0.2606
30	—	—	0.2210	0.3906	0.8348	0.39132	0.8348	0.3913
40	—	—	0.2228	0.5201	0.8347	0.5219	0.8347	0.5219
50	—	—	0.2245	0.6492	0.8346	0.65256	0.8346	0.6525
60	—	—	0.2263	0.7780	0.83446	0.7831	0.83446	0.7831

Here, $(-\Delta H_r)$ is the heat of the reaction, U is the heat transfer coefficient, and T_w is the surrounding temperature. The above equation may be rearranged using eqs. (1.3) of Table I and (28). They may be written as follows:

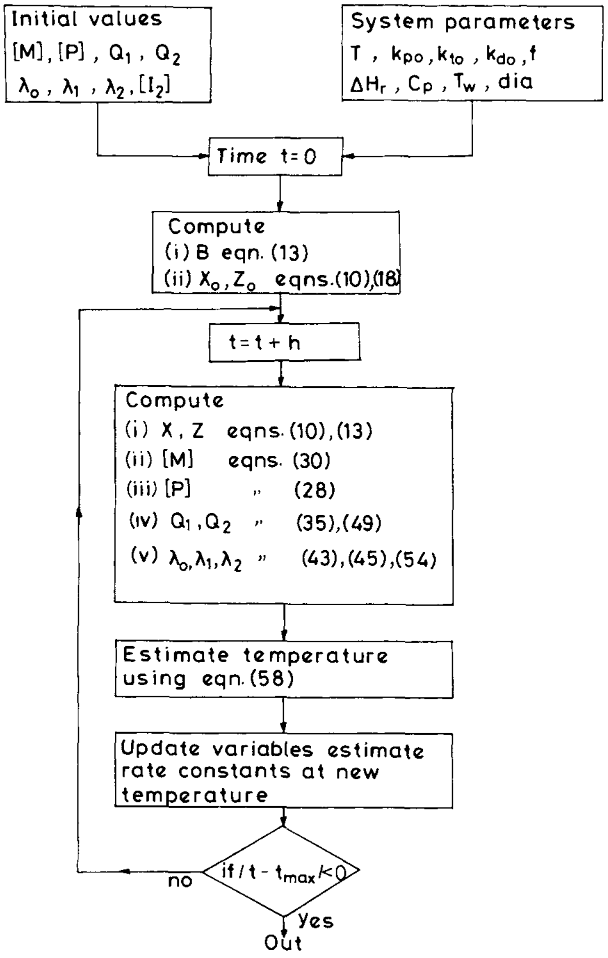

Figure 2 Semianalytical scheme based on this work for free radical polymerization.

Table III Rate Constants and Other Parameters for PMMA[22,43]

A $= 0.168 - 8.21 \times 10^{-6} (T - T_{gP})^2$
B $= 0.03$
C_p = 0.4 cal/gm°C
E_d = 30.66 Kcal/mol
E_p = 4.35 Kcal/mol
E_t = 0.701 Kcal/mol
E_γ = 4.09 Kcal/mol
$E_{\theta p}$ = 28.2 Kcal/mol
$E_{\theta t}$ = 34.4 Kcal/mol
f = 0.58
$\Delta \bar{H}_r$ = 13.9 Kcal/mol
$k_d^o = 6.32 \times 10^{16}$ min^{-1}
$k_t^o = 5.88 \times 10^9$ L/mol min
$k_p^o = 2.95 \times 10^7$ L/mol min
$k_\gamma^o = 3.956 \times 10^{-4}$
T_{gP} = 387 K
$\theta_p^o = 5.4814 \times 10^{-16}$ min
$\theta_t^o = 1.1553 \times 10^{-227}$ mol min/L
ρ_m = 0.9665–0.0011 (T–273) gm/cm^3
ρ_p = 1.2 gm/cm^3
$[I_2]_o$ = 0.0258 gmol/L
$[M]_0$ = 89334 gmol/L

$$k_t = \frac{k_{to} D_o}{D_o + k_{to} \theta_t \lambda_o} \quad \text{(gel effect)} \tag{2.1}$$

$$k_p = \frac{k_{po} D_o}{D_o + k_{po} \theta_p \lambda_o} \quad \text{(glass effect)} \tag{2.2}$$

where

$$\theta_t = \frac{\theta_t^o}{[I_2]} \exp (E_{\theta t}/RT) \tag{2.3}$$

$$\theta_p = \theta_p^o \exp (E_{\theta p}/RT) \tag{2.4}$$

$$D_o = \left[\frac{2.303(1 - \phi_p)}{A + B(1 - \phi)} \right] \tag{2.5}$$

$$\gamma = \frac{k_{tc}}{k_{td}} = k_\gamma^o \exp (E_\gamma/RT) \tag{2.6}$$

Table IVA Results of Isothermal Polymerization without Gel Effect[a]

Time	$[M] \times 10^{-7}$	$[P] \times 10^{7}$	$Q_1 \times 10^{3}$	Q_2	$\lambda_o \times 10^{3}$	λ_1	$\lambda_2 \times 10^{-4}$	*PDI*
10	0.8631	0.834	0.1745	0.7297	0.1306	0.3019	0.1386	1.9851
	(0.8632)	(0.834)	(0.1745)	(0.7297)	(0.1305)	(0.3016)	(0.1385)	(1.9864)
20	0.8340	0.8328	0.1686	0.6822	0.2608	0.5933	0.2682	1.9869
	(0.8341)	(0.8328)	(0.1686)	(0.6823)	(0.2607)	(0.5930)	(0.2680)	(1.9873)
30	0.8059	0.8317	0.1629	0.6379	0.3907	0.8746	0.3892	1.9879
	(0.8060)	(0.8317)	(0.1629)	(0.6380)	(0.3905)	(0.8741)	(0.3890)	(1.9882)
40	0.7788	0.8305	0.1574	0.5965	0.5203	1.1461	0.5022	1.9892
	(0.7788)	(0.8305)	(0.1574)	(0.5966)	(0.520)	(1.1454)	(0.5019)	(1.9895)
50	0.7525	0.8294	0.1521	0.5579	0.6495	1.4081	0.6077	1.9908
	(0.7527)	(0.8294)	(0.1521)	(0.5580)	(0.6492)	(1.4072)	(0.6074)	(1.9910)
60	0.7273	0.8283	0.1470	0.5218	0.7784	1.6610	0.7063	1.9929
	(0.7274)	(0.8283)	(0.1470)	(0.5219)	(0.7780)	(1.6599)	(0.7059)	(1.9930)

[a] Results in paranthesis are numerical computations with $\Delta t = 0.0001$ min.

$$\frac{dy}{dx} + \beta y = \alpha e^{-mx} \tag{57}$$

where

$$Y = T\text{-}T_W \quad \text{(a)}$$

$$X = Z_0 - Z \quad \text{(b)}$$

$$\beta = \frac{8U}{D\rho C_p f k_d Z_0} \quad \text{(c)}$$

$$\alpha = \frac{(-\Delta H_r)[M]_0\, m}{\rho C_p} \quad \text{(d)} \qquad (58)$$

The integrating factor of eq. (58) is $e^{\beta x}$. Using the initial condition $T = T_0$ at $x = 0$, we obtain the following solution.

$$T\text{-}T_W = \frac{\alpha e^{-m(Z_0-Z)}}{(\beta - m)} + (T_0\text{-}T_W)e^{-\beta(Z_0-Z)} - \frac{\alpha e^{-\beta(Z_0-Z)}}{(\beta - m)} \tag{59}$$

This result has been built in the algorithm in Figure 2.

Table IVB Results of Nonisothermal Polymerization without Gel Effect[a]

Time (min)	Temp. °K	$[M] \times 10^{-1}$ $\frac{\text{gmol}}{\text{L}}$	$[P] \times 10^{7}$ $\frac{\text{gmol}}{\text{L}}$	$Q_1 \times 10^{3}$	Q_2	$\lambda_o \times 10^{3}$	λ_1	$\lambda_2 \times 10^{4}$	*PDI*
10	331.32	0.8687	0.6631	0.1707	0.8791	0.09047	0.2454	0.1329	1.9897
	(331.49)	(0.8662)	(0.7529)	(0.1707)	(0.7742)	(0.1142)	(0.2718)	(1.1332)	(1.9864)
20	331.27	0.8462	0.6575	0.1662	0.8595	0.1716	0.4714	0.2575	1.982
	(331.44)	(0.8405)	(0.749)	(0.1665)	(0.7315)	(0.2151)	(0.5218)	(0.2572)	(1.9863)
30	331.23	0.8244	0.6531	0.1617	0.8013	0.2515	0.6893	0.3755	1.9876
	(331.39)	(0.8159)	(0.7456)	(0.1605)	(0.6912)	(0.3191)	(0.7749)	(0.3736)	(1.987)
40	331.184	0.8034	0.6487	0.1575	0.7648	0.3303	0.900	0.4874	1.9874
	(331.342)	(0.7920)	(0.7423)	(0.1557)	(0.6531)	(0.4221)	(0.1013)	(0.4835)	(1.9874)
50	331.146	0.7830	0.6446	0.1534	0.7302	0.40809	0.1104	0.5936	1.9876
	(331.296)	(0.7689)	(0.7392)	(0.1510)	(0.6174)	(0.5242)	(0.1243)	(0.5868)	(1.9883)
60	331.110	0.7533	0.6407	0.1495	0.6772	0.4849	0.1301	0.6942	1.988
	(331.252)	(0.7467)	(0.7361)	(0.1466)	(0.5837)	(0.6254)	(0.1466)	(0.68403)	(1.989)

[a] Results in parenthesis are numerical computations with $\Delta t = 0.0001$ min. $U = 2.0343 \times 10^{-3} \frac{\text{Kcal}}{\text{h cm}^2\text{c}}$; Dia = 2.0 cm.

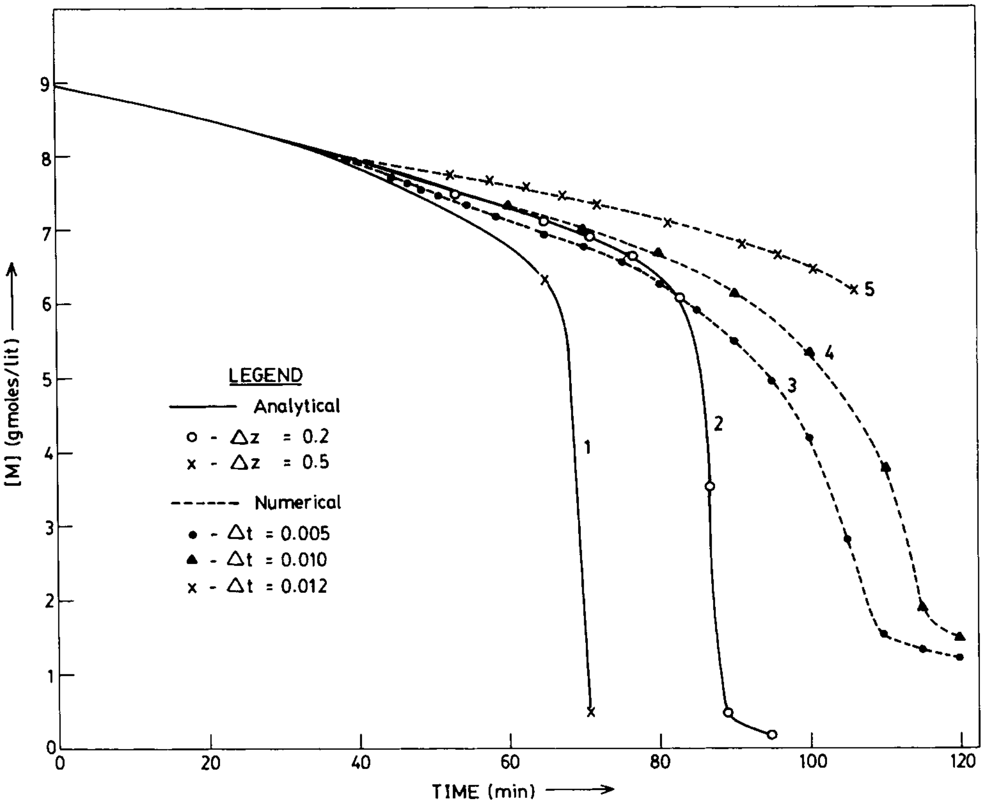

Figure 3 $[M]$ vs. t for isothermal polymerization (T = 333°K) with gel effect. Star indicates numerical instability.

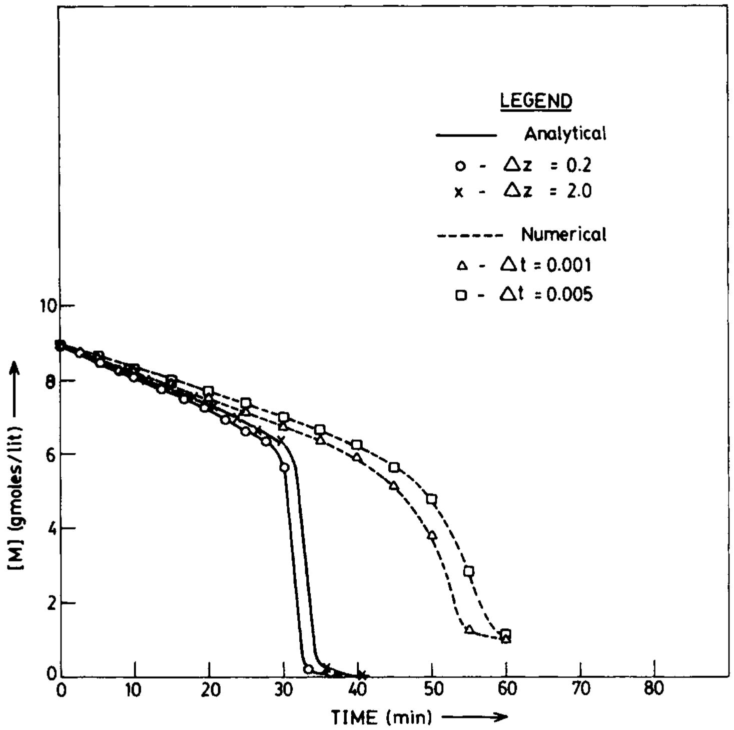

Figure 4 $[M]$ vs. t for isothermal polymerization (T = 343°K) with gel effect. Star indicates numerical instability.

RESULTS AND DISCUSSION

We have considered the simulation of batch reactor carrying out free radical polymerization. The reaction mass consists of unreacted monomer M, initiators I_2, polymer radicals P_n ($n = 1, 2 \cdots$), and dead polymer chains, M_n ($n = 2, 3, \cdots$). The mole balance relations for these species are given in Table I and they are seen to involve fives rate constants k_d, k_p, k_{tc}, k_{td}, and k_{tr}. To reduce the computational task, we have developed the moment relations; these are also given in Table I. These moment relations are an infinite set of differential equations; their numerical integration is difficult because of several reasons, which follow.

Let us first consider the polymerization of methyl methacrylate using benzoyl peroxide initiator and various rate constants that are summarized in Table III. It is found that the termination rate constants, k_{tc} and k_{td}, are both dependent upon the zeroth and the first moments of polymer in addition to temperature and the fall of rate constants with conversion is attributed to the gel effect. Similarly, the propagation rate constant k_p also is reduced due to the glassy effect. For short times of polymerization, these rate constants could be taken as time invariant. Rough computations show that for short times, the molar concentration of polymer radicals, $[P]$, is of the order of 10^{-8}, monomer concentration, $[M]$, of the order of 10, while the reactor temperature is of the order of 10^2. Due to the wide variation in the ranges of various reactor parameters, the differential equations of Table I are numerically "stiff" and require selection of a very small time increment Δt. In order to remove this numerical stiffness, in this work we have attempted to adopt the analytical solution, developed for invariant rate, as follows.

It is observed that all computational schemes, im-

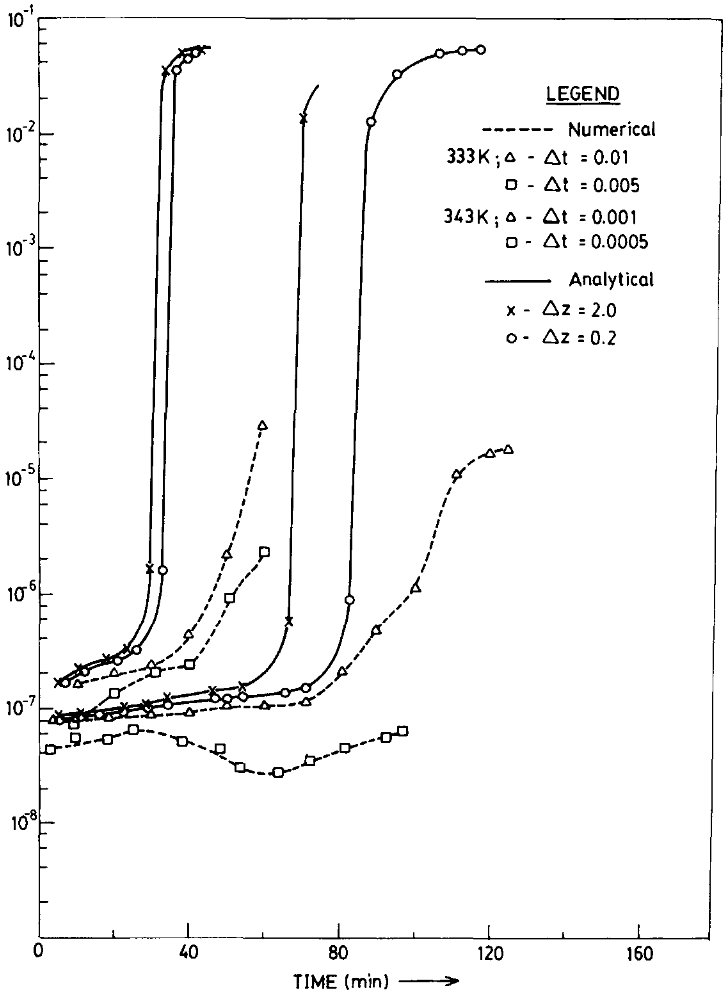

Figure 5 $[P]$ vs. time for isothermal polymerization with gel effect. Star indicates numerical instability.

plicits or otherwise, divide the total polymerization time, t, into small incremental times, Δt. Between these incremental times, the process variables are assumed to be constant at some value and the slopes of the variation of these process variables is evaluated. In the Runge–Kutta computations, the slopes are computed at four points and their averages are computed to determine the values of the process variables at the end of the incremental times. A successive repetition of this method leads to the complete numerical solution seen in the flow chart of Figure 1.

Using the Runge–Kutta numerical technique of Figure 1, we have developed the numerical solution of polymerization of methyl methacrylate in batch reactors. We find that the numerical results depend upon the value of Δt chosen, and we have summarized some of the results in Table II. For large Δt, results are found to diverge, whereas for $\Delta t \sim 0.0001$, numerical values become independent of the choice of Δt. We have subsequently found the numerical solutions for following cases.

Case 1. Isothermal polymerization without the gel effect (i.e., $k_t = k_{t0}$) and glass effect (i.e., $k_p = k_{p0}$). Temperatures of the reactor is 333°K.

Case 2. Isothermal polymerization with the gel and glass effects (k_t and k_p given in Table III). Reactor temperature is 333°K, 343°K and 363°K.

Case 3. Nonisothermal polymerization without the gel effect (i.e., $k_t = k_{t0}$) and glass effect (i.e., $k_p = k_{p0}$). Initial temperature is 333°K.

Case 4. Nonisothermal polymerization with the gel and glass effects (k_t and k_p given in Table III). Initial temperature is 333°K.

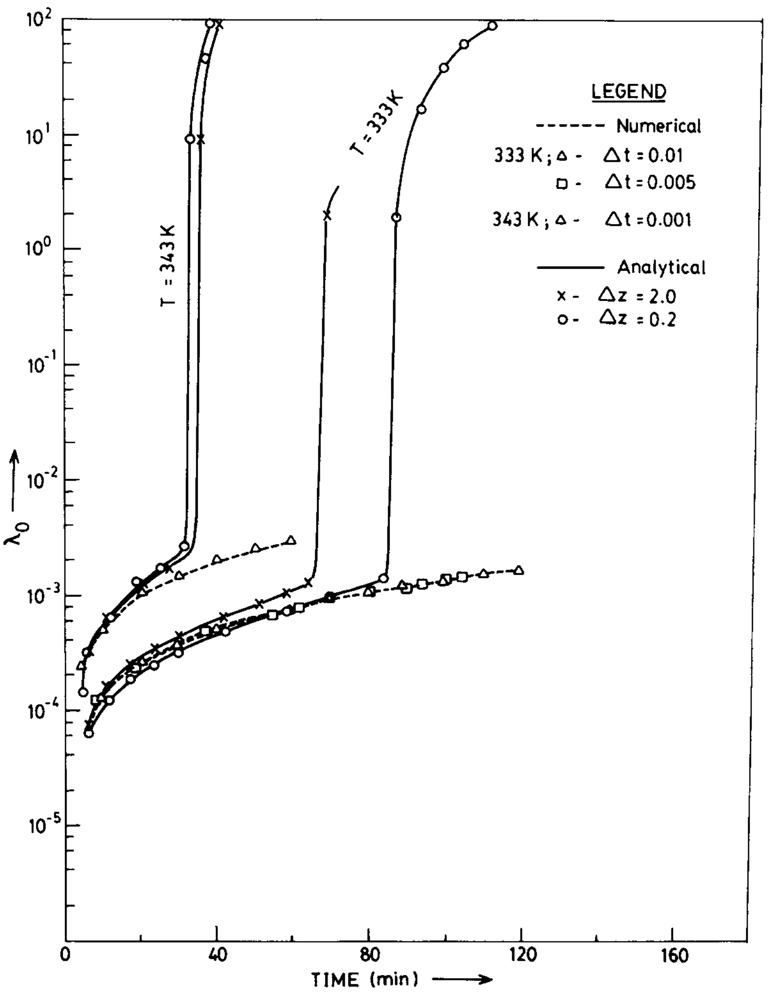

Figure 6 λ_0 vs. time for isothermal polymerization with gel effect. Star indicates numerical instability.

We have also prepared a computer program, with the flow sheet in Figure 2, in which we have computed the results using the analytical solution between a given time increment instead of evaluating the slopes as done earlier. In Table IV (A and B), we have given the results derived from the Runge–Kutta technique as well as from the analytical scheme for Case 1 computations. A total match of results confirms that the analytical expressions derived in this work are free from any error.

In Case 2 computations, we assume the batch reactor to be isothermal, but rate constants, k_p, k_{tc}, and k_{td}, are allowed to drift due to the glass and gel effects according to Table III. It is found that after a certain time of polymerization, the rate constants k_p and k_t decrease in value and the monomer is consumed at a rapid rate. In Figure 3, $[M]$ vs. t, derived from the Runge-Kutta technique, has been plotted for $\Delta t = 0.01, 0.012$, and 0.005. For Δt less that 0.005, results merge with curve 3; however for Δt larger than this, there is an overflow in computation. Also in Figure 3 is shown the results found from semianalytical approach developed here in Z-domain; we found that for ΔZ less than 0.2, results overlap with curve 2, while for larger ΔZ, the point where sharp rise in conversion occurs is preponed. The comparison of curves 2 and 3 in Figure 3 shows that the results are close to each other for short times, whereas for large times the semianalytical solution predicts sharper and earlier gelation. Similar $[M]$ vs. t is observed at higher temperature, as shown in Figure 4. Figures 5 and 6 give the numerical as well as semianalytical results for $[P]$ vs. t and λ_0 vs. t, respectively. The increase in the values of $[P]$ and λ_0 are found to be considerably sharper for the latter, and this perhaps is responsible for what observations made in Figures 3 and 4. We have similarly presented results for λ_1 and λ_2 vs. t in Figures 7 and 8. The difference between the numerical and semianalytical decreases as higher moments increase, and λ_2 results are essentially similar. Generally, in numerical computations, no matter what Δt is chosen the results become unstable as the end of the computation is approached. This is because $[P]$ begins to fall and

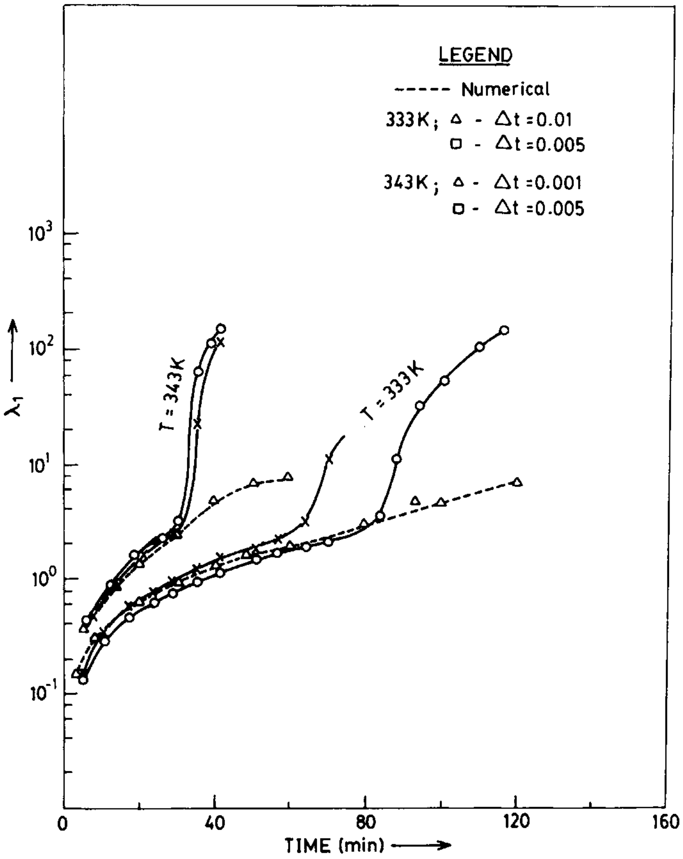

Figure 7 λ_1 vs. time for isothermal polymerization with gel effect. Star indicates numerical instability.

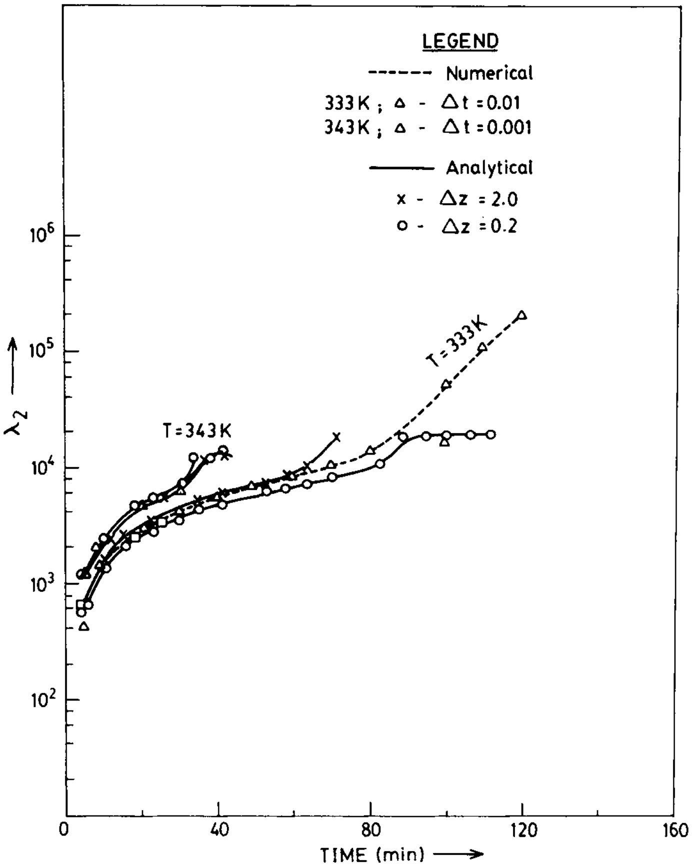

Figure 8 λ_2 vs. time for isothermal polymerization with gel effect. Star indicates numerical instability.

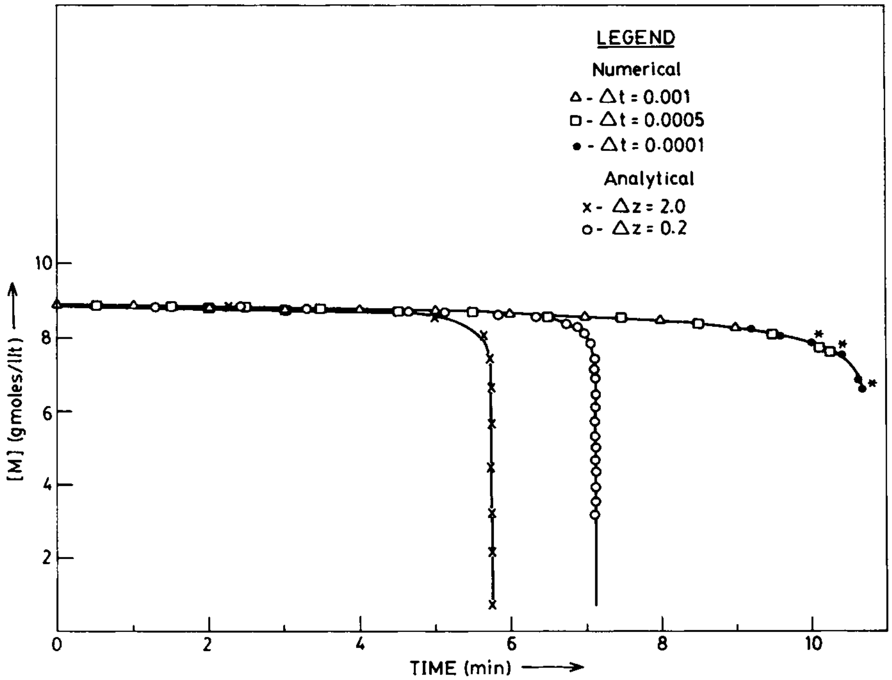

Figure 9 [*M*] vs. time for nonisothermal polymerization without gel effect. Star above indicates instability in R.K. technique.

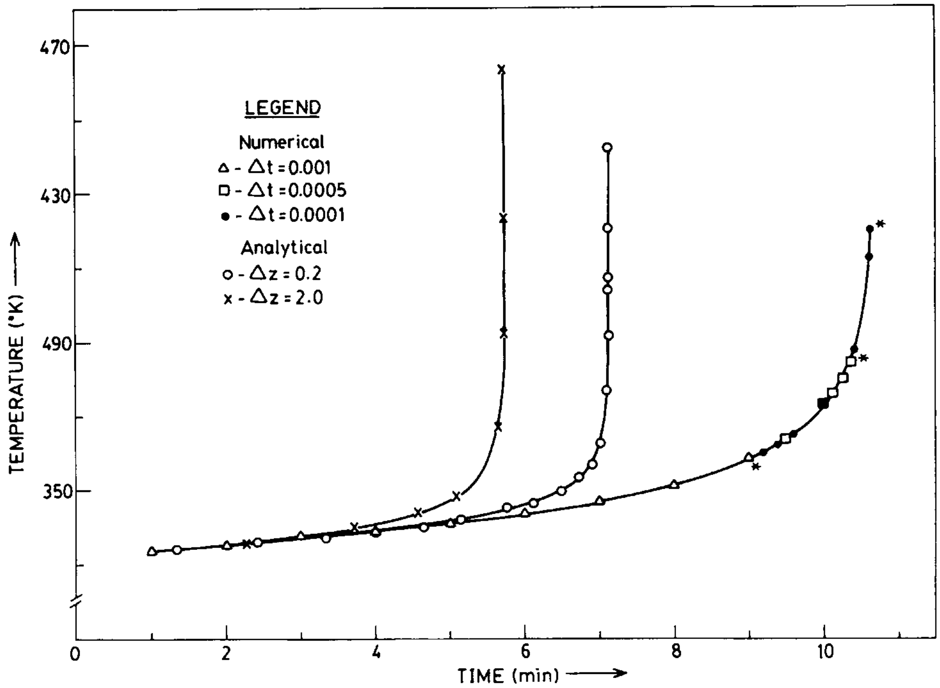

Figure 10 Temperature vs. time for nonisothermal polymerization without gel effect. Star above indicates instability in R.K. technique.

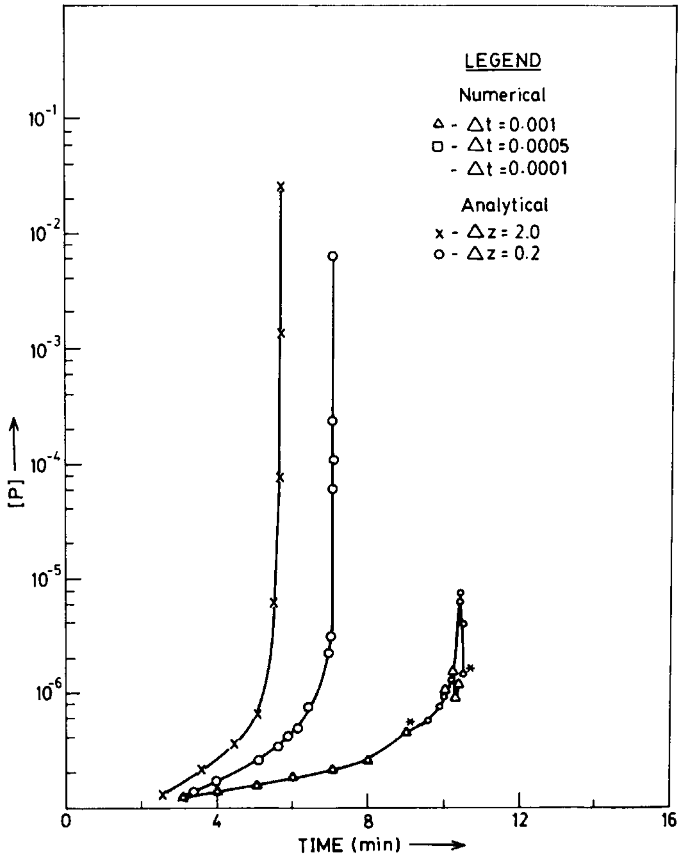

Figure 11 $[P]$ vs. time for nonisothermal polymerization without gel effect. Star above indicates numerical instability.

near the end it becomes negative, which leads to a numerical overflow.

Computation for Cases 3 and 4 require additional energy balance equations, which must be solved simultaneously. The semianalytical as well as the numerical results for Case 3 are shown in Figures 9 to 15. Figure 9 gives $[M]$ vs. t and, for short times, the results are almost identical. The point of gelation for numerical results is always characterized by an overflow. On the other hand, there is never an instability in the semianalytical, even though the time of gelation is predicted to be lower than those predicted through the numerical technique. The temperature, T, vs. t in Figure 10 also shows a point of sharp rise and corresponds to point of gelation in $[M]$ vs. plot in Figure 9. The $[P]$ vs. t in Figure 11, λ_0 vs. t in Figure 12, λ_1 vs. t in Figure 13, λ_2 vs. t in Figure 14, and Q_2 vs. t in Figure 15 behave similarly.

The general case of nonisothermal polymerization with gel and glass effect (i.e., Case 4) has also been analyzed and the results have been presented in Figures 16 to 22. As found earlier, the match between the numerical and semianalytical is excellent for short times. For the latter, as ΔZ is increased, the time of gelation is found to decrease, whereas for the numerical, the time of gelation is larger and the results always undergo an overflow. It appears (Figure 18) that the value of $[P]$ predicted by semianalytical technique is of a larger order of magnitude and when the gelation occurs, the rise in $[P]$ is also very steep. It is likely that the Runge–Kutta technique is not good enough to pick up this fast rise and this may be responsible for the discrepancy in results.

CONCLUSIONS

The simulation of free radical polymerization has been carried out extensively in the past and is known to take considerable computer time due to stiffness of differential equations governing the zeroth, first,

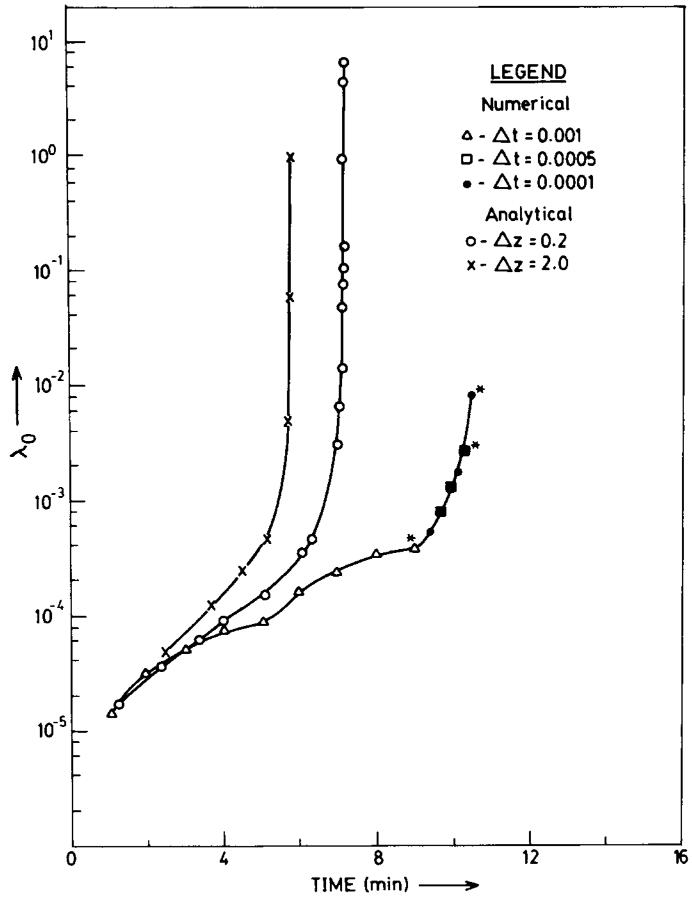

Figure 12 λ_0 vs. time for nonisothermal polymerization without gel effect. Star indicates numerical instability.

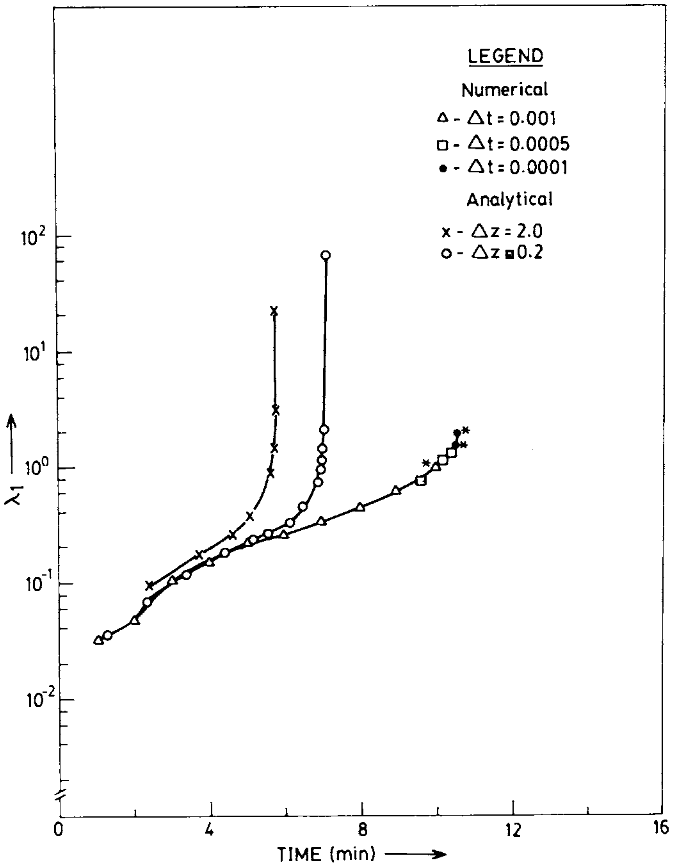

Figure 13 λ_1 vs. time for nonisothermal polymerization without gel effect. Star indicates numerical instability.

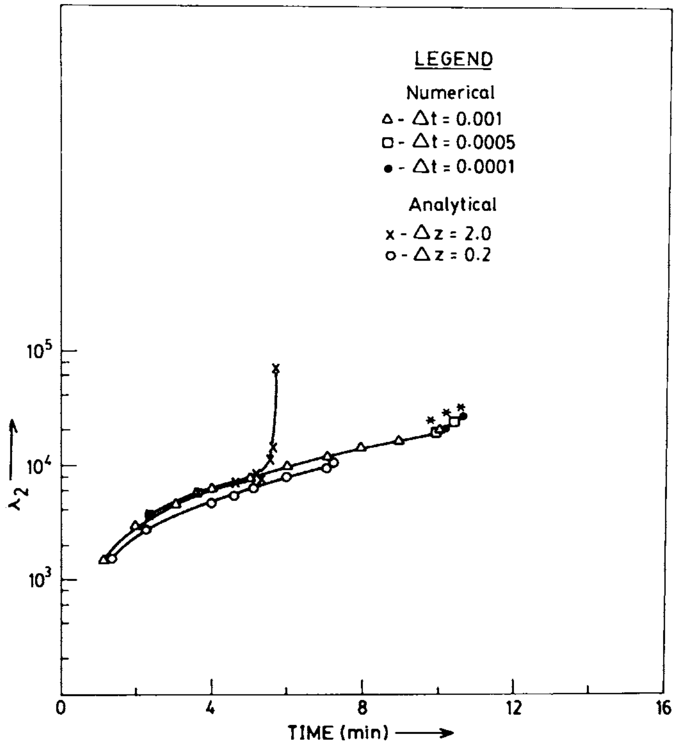

Figure 14 λ_2 vs. time for nonisothermal polymerization without gel effect. Star indicates numerical instability.

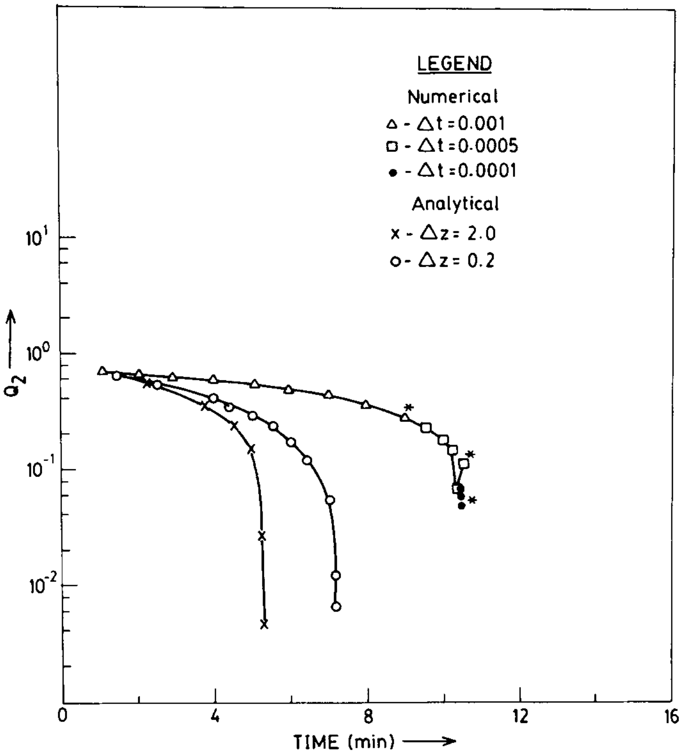

Figure 15 Q_2 vs. time for nonisothermal polymerization without gel effect. Star indicates numerical instability.

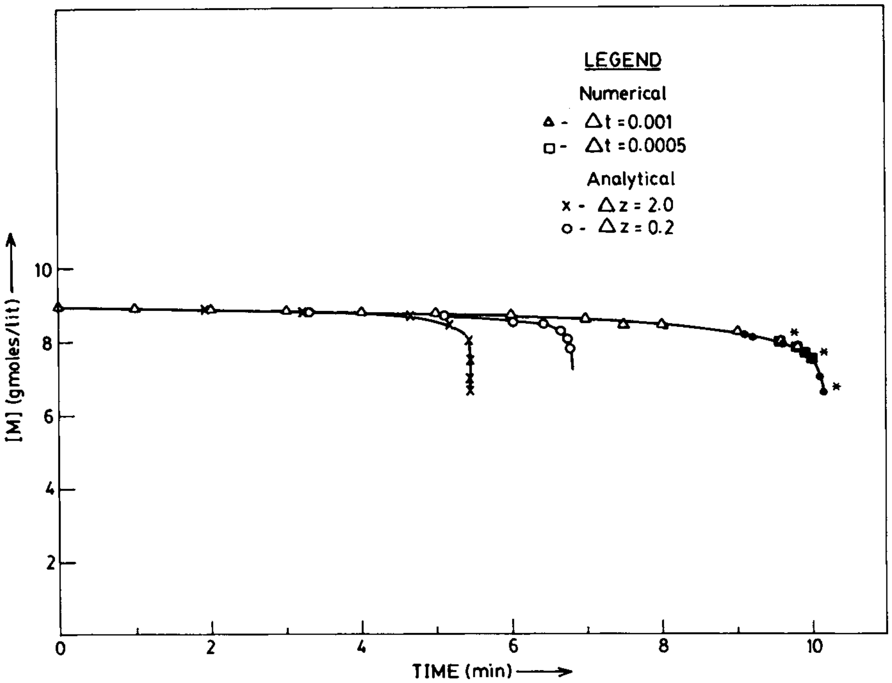

Figure 16 $[M]$ vs. time for nonisothermal polymerization with gel effect. Star indicates numerical instability.

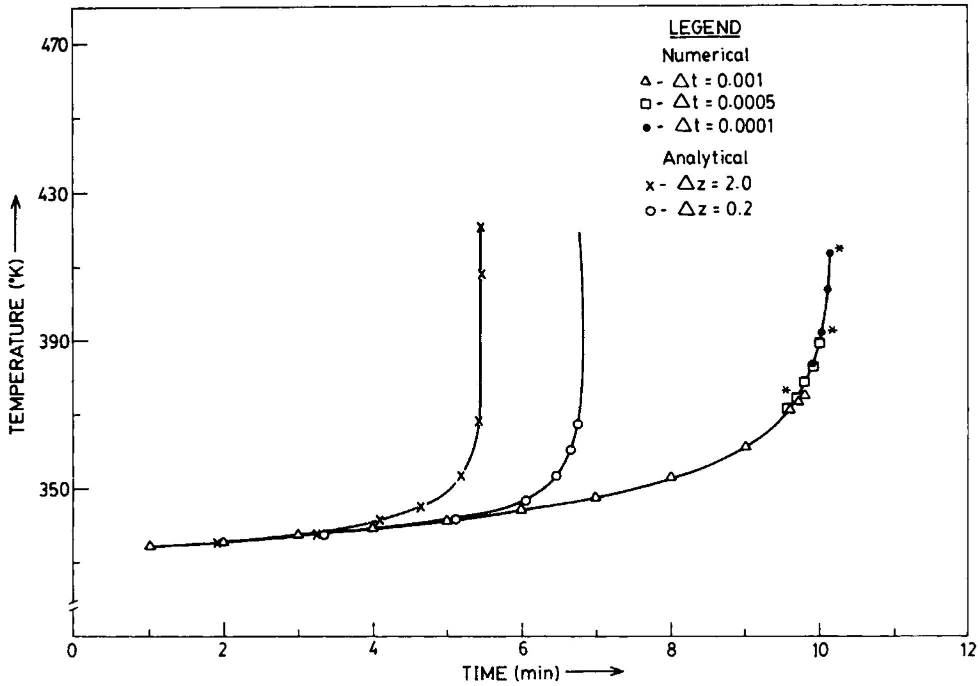

Figure 17 T vs. time for nonisothermal polymerization with gel effect. Star indicates numerical instability.

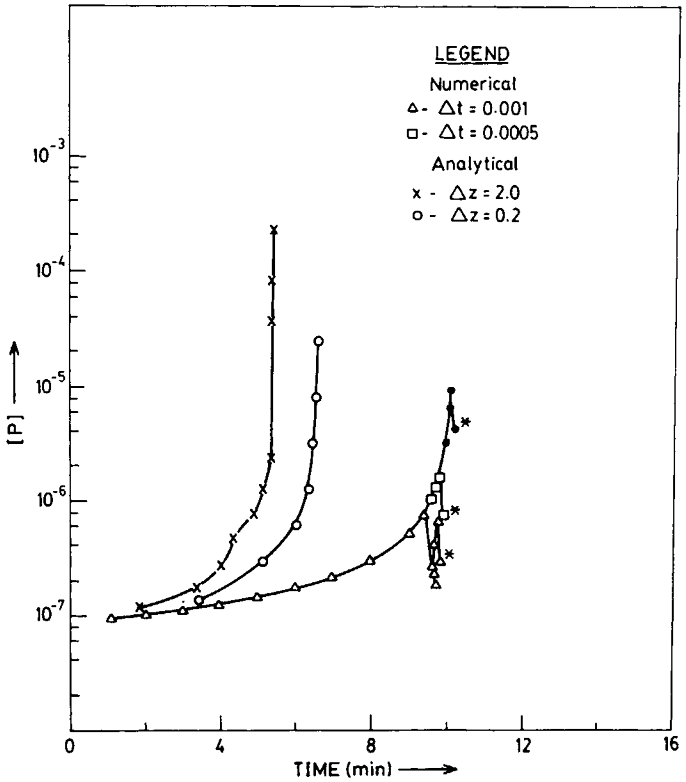

Figure 18 $[P]$ vs. time for nonisothermal polymerization with gel effect. Star indicates numerical instability.

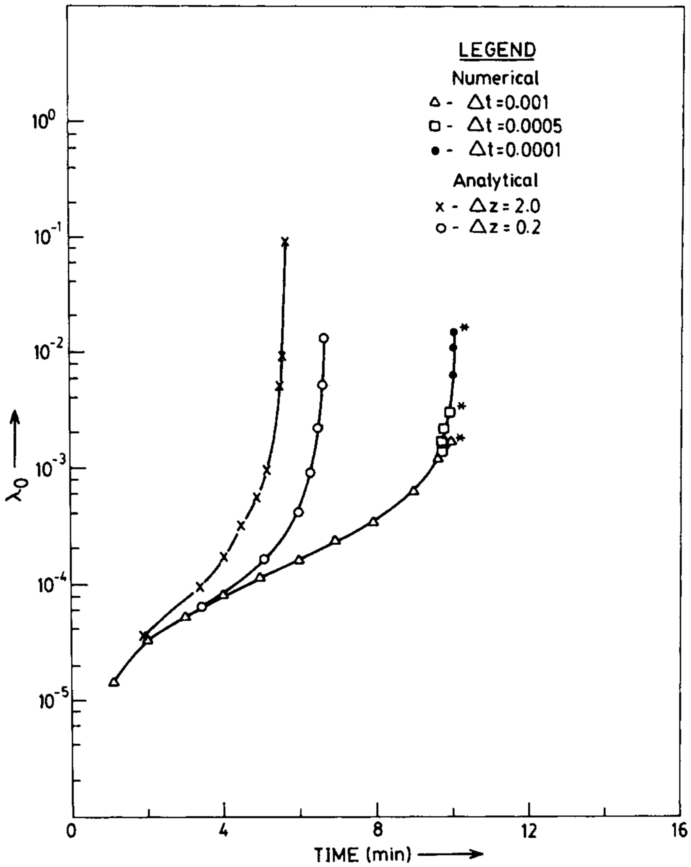

Figure 19 λ_0 vs. time for nonisothermal polymerization with gel effect. Star indicates numerical instability.

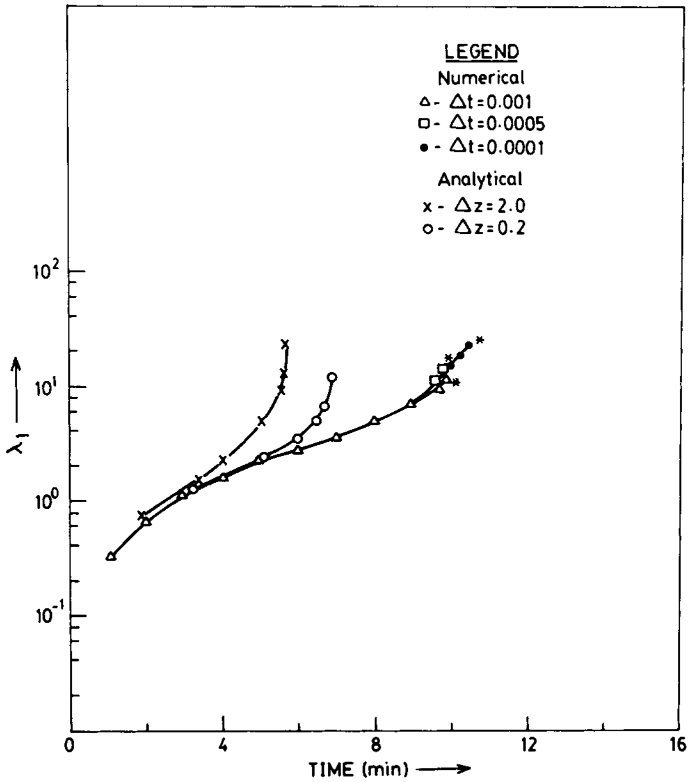

Figure 20 λ_1 vs. time for nonisothermal polymerization with gel effect. Star indicates numerical instability.

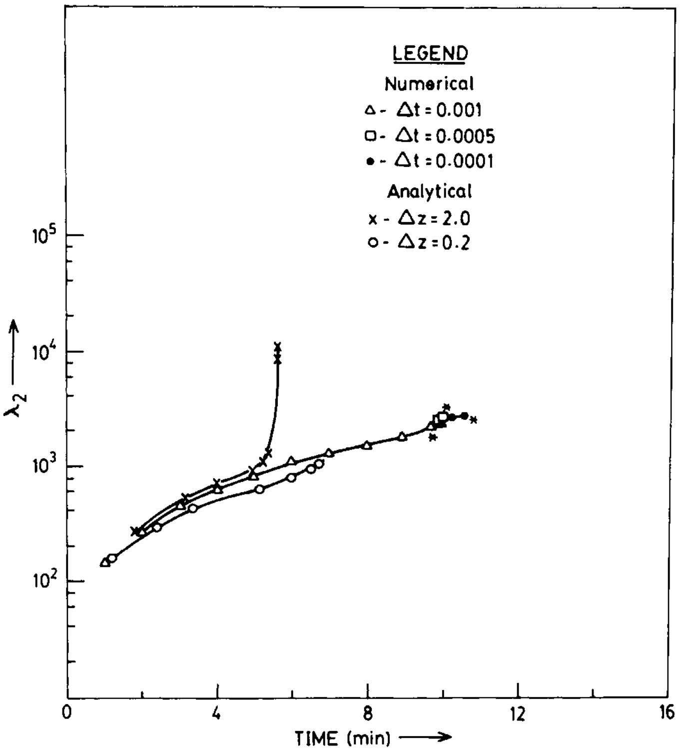

Figure 21 λ_2 vs. time for nonisothermal polymerization with gel effect. Star indicates numerical instability.

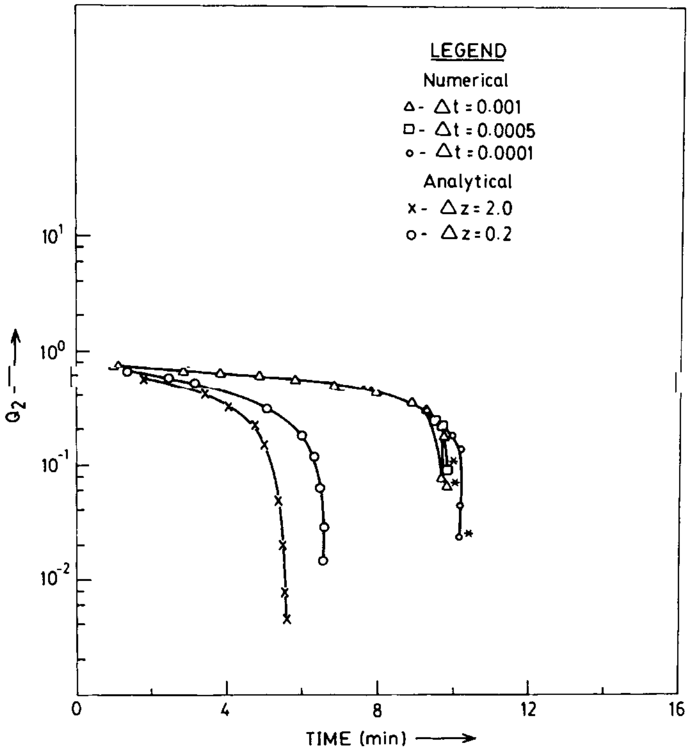

Figure 22 Q_2 vs. time for nonisothermal polymerization with gel effect. Star indicates numerical instability.

and second moments of free radicals. These relations are nonlinear in nature, but it was possible to transform them into the Z-domain, where they are linear for time invariant rate constants. This transformation is possible only when the reactor is operated isothermally and the analytical solution for these has been developed in this work.

It was further realized that while solving the reactor performance numerically (using any technique, e.g., fourth order Runge–Kutta), between any given time increment, the reactor is indeed assumed isothermal and, with this assumption, the differential equations are assumed to give approximately the same result as the difference equation.

We have developed a computer program to calculate the performance of nonisothermal reactor in presence of gel effect using the analytical solution developed above. We have also found the solution numerically using the fourth order Runge–Kutta technique. We find that the semianalytical approach always gives stable results under all variations of parameters studied while the Runge–Kutta technique, under similar parameters, diverges in the end. It was found that the numerical integration of differential equations could not compute the fast change in $[P]$, Q_1, and Q_2 accurately and the solution diverged as a result of this. In addition, the semianalytical approach adopted in this work is computationally efficient and can be adopted on any personal computer.

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APPENDIX I

Rigorous Solution of Dead Polymer and Radical Moments

We have assumed that $Z = Z_0$ in eqs. (42), (48), and (52) in the derivation of equations for λ_0, Q_2, and λ_2. The rigorous solution for the above distributions is given here.

We find that in the derivation of the equations for dead polymer and polymer radical distributions, the integral,

$$I = \int \frac{e^{-a(Z_0-Z)}}{Z} dZ \tag{A1.1}$$

arises naturally.

Making use of the transformation $Z_0 - Z = u$, we can write

$$\begin{aligned} I &= -\int \frac{e^{-au}}{(Z_0 - u)} du \\ &= -\frac{1}{Z_0}\left[\sum_{n=0}^{\infty} \frac{1}{Z_0^n} \int u^n e^{-au} du\right] \end{aligned} \tag{A1.2}$$

Since

$$\int u^n e^{au} du = e^{au} \sum_{r=0}^{n} \frac{(-1)^r n!\, u^{n-r}}{(n-r)!\, a^{r+1}} \tag{A1.3}$$

we get the integral as

$$I = e^{-a(Z_0-Z)} \sum_{r=0}^{n} \frac{1}{Z_0^{n+1}} \sum_{r=0}^{n} \frac{n!\,(Z_0 - Z)^{n-r}}{(n-r)!\, a^{r+1}} \tag{A1.4}$$

The zeroth moment, λ_0, is therefore given by

$$\begin{aligned} \int d\lambda_0 = -\frac{(0.5k_{tc} + k_{td})mk_d}{2k_pk_t} \int Z \\ \times \frac{1 - \psi e^{-2}(Z_0 - Z)}{1 + \psi e^{-2}(Z_0 - Z)} dZ + [S] + \text{Const.} \end{aligned}$$

We can write

$$\begin{aligned} &\int Z \frac{1 - \psi e^{-2(Z_0-Z)}}{1 + \psi e^{-2(Z_0-Z)}} dZ \\ &\quad = -Z_0 \int \frac{1 - \psi e^{-2(Z_0-Z)}}{1 + \psi e^{-2(Z_0-Z)}} d(Z_0 - Z) \\ &\qquad + \int (Z_0 - Z) \frac{1 - \psi e^{-2(Z_0-Z)}}{1 + \psi e^{-2(Z_0-Z)}} d(Z_0 - Z) \end{aligned}$$

consider the integral,

$$\begin{aligned} &\int (Z_0 - Z) \frac{1 - \psi e^{-2(Z_0-Z)}}{1 + \psi e^{-2(Z_0-Z)}} d(Z_0 - Z) \\ &\qquad = \int X \frac{1 - \psi e^{-2X}}{1 + \psi e^{-2X}} dX \end{aligned}$$

This can be integrated by parts by assuming

$$\begin{aligned} V &= \int \frac{1 - \psi e^{-2X}}{1 + \psi e^{-2X}} dX \\ &= \int \left(1 - \frac{2\psi e^{-2X}}{1 + \psi e^{-2X}}\right) dX \\ V &= X + ln[1 + \psi e^{-2X}] \end{aligned}$$

$$\int V du = \int [X + ln\left(1 + \psi e^{-2X}\right)] dX \tag{A1.5}$$

However, we know that

$$\int \frac{ln(a+bX)}{X}\,dX$$

cannot be expressed as a finite combination of elementary functions.[48] Therefore, we express the term involving logarithmic function as a series

$$\therefore ln(1+y) = \sum_{n=1}^{\infty} (-1)^{n+1}\frac{Y^n}{n}$$

where $Y = \psi e^{-2X}$
Therefore,

$$\int V du = \frac{X^2}{2} + \int \left(\psi e^{-2X} - \frac{\psi^2 e^{-4X}}{2} + \frac{\psi^3 e^{-6X}}{3} - \cdots\right) dX$$

$$= \frac{X^2}{2} + \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n e^{-2nX}}{2n^2} \quad \text{(A1.6)}$$

Hence, we get

$$\int X \frac{1-\psi e^{-2X}}{1+\psi e^{-2X}}\,dX = \frac{X^2}{2} + Xln(1+\psi e^{-2X}) - \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n e^{-2nX}}{2n^2} \quad \text{(A1.7)}$$

It is also seen that

$$-Z_0 \int \frac{1-\psi e^{-2(Z_0-Z)}}{1-\psi e^{-2(Z_0-Z)}}\, d(Z_0 - Z) = -Z_0 V$$

$$= -Z_0(x + ln(1+\psi e^{-2X})) \quad \text{(A1.8)}$$

writing

$$\Delta = (0.5k_{tc} + k_{td})\frac{mk_d}{2k_p k_t}$$

we have

$$\lambda_0 = \Delta\left[\frac{1}{2}(Z_0^2 - Z^2) + Zln(1+\psi e^{-2(Z_0-Z)}) + \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n e^{-2n(Z_0-Z)}}{2n^2}\right] + [S] + C_1^*$$

$$\text{(A1.9)}$$

where C_1^* is the constant of integration to be evaluated using the initial condition, $\lambda_0 = \lambda_{00}$ at $t = 0$ (or $Z = Z_0$).
We get,

$$C_1^* = \lambda_{00} - \Delta\left[Z_0 ln(1+\psi) + \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n}{2n^2}\right] - [S]_0$$

Hence, we finally obtain

$$\lambda_0 - \lambda_{00} = \Delta\left[\frac{1}{2}(Z_0^2 - Z^2) + ln\left\{\frac{(1+\psi e^{-2(Z_0-Z)Z}}{(1+\psi)^Z 0}\right\} - \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n}{2n^2} \times (1 - e^{-2n(Z_0-Z)})\right] + ([S] - [S]_0) \quad \text{(A1.10)}$$

The equation for second moment of polymer radical distribution (from Eq. 46) is

$$Q_2\left(\frac{[M]}{[M]_0}\right)^{-1/m} = \int \left(\frac{[M]}{[M]_0}\right)^{-1/m} (2fk_d[I_2] + 2k_p[M]Q_1 + k_p[M][P])dt$$

This can be split into three integrals, as

$$Q_2\left(\frac{[M]}{[M]_0}\right)^{-1/m} = \int (2fk_d[I_2]\left(\frac{[M]}{[M]}\right)^{-1/m} dt + \int 2k_p[M]Q_1\left(\frac{[M]}{[M]}\right)^{-1/m} dt + \int \left(\frac{[M]}{[M]}\right)^{-1/m} k_p[M][P]dt \quad \text{(A.1.11)}$$

The first integral, I_1, gives

$$I_1 = \frac{k_d}{2k_t}(Z+1) \quad \text{(A1.12)}$$

The second integral I_2 is

$$I_2 = \int \left(\frac{[M]}{[M]_0}\right)^{-1/m}\left[2k_p[M]_0 C_1\left(\frac{[M]}{[M]_0}\right)^2 + 2k_p[M]_0 C_2\left(\frac{[M]}{[M]_0}\right)^{1+1/m} + \frac{k_d}{2k_t}(Z+1)2k_p[M]_0\left(\frac{[M]}{[M]_0}\right)\right]dt$$

Expressing $\left(\frac{[M]}{[M]_0}\right)$ in terms of $(Z_0 - Z)$, making use of eq. (A1.4), and dividing by the integrating factor, we obtain for the second integral

$$I_2 = -\frac{4k_p[M]_0C_1}{k_d} e^{-2m(Z_0-Z)} \sum_{n=0}^{\infty} \frac{1}{Z_0^{n+1}} \times \sum_{r=0}^{n} \frac{n!\,(Z_0-Z)^{n-r}}{(n-r)!\,(2m-1)^{r+1}} - \frac{4k_p[M]_0C_2}{k_d} \times e^{-(m+1)(Z_0-Z)} \sum_{n=0}^{\infty} \frac{1}{Z_0^{n+1}} \sum_{r=0}^{n} \frac{n!\,(Z_0-Z)^{n-r}}{(n-r)!\,m^{r+1}} - \frac{2k_p[M]_0}{k_t}\left[\frac{e^{-(m)(Z_0-Z)}}{(m-1)}\right] - \frac{2k_p[M]_0}{k_t} e^{-(m)(Z_0-Z)} \times \sum_{n=0}^{\infty} \frac{1}{Z_0^{n}} \sum_{r=0}^{n} \frac{n!\,(Z_0-Z)^{n-r}}{(n-r)!\,(m-1)^{r+1}} \quad \text{(A1.13)}$$

Similarly, the third integral I_3 is

$$I_3 = -\frac{[M]_0}{1-\frac{1}{m}}\left(\frac{[M]}{[M]_0}\right) \quad \text{(A1.14)}$$

For the sake of convenience, let

$$\sum^{2} (X) = \sum_{n=0}^{\infty} \frac{1}{Z_0^{n+1}} \sum_{r=0}^{n} \frac{n!\,(Z_0-Z)^{n-r}}{(n-r)!\,X^{r+1}} \quad \text{(A1.15)}$$

Then

$$Q_2 = \frac{k_d}{2k_t}(Z+1) - \frac{4k_p[M]_0C_1}{k_d} e^{-2m(Z_0-Z)} \times \sum^{2} (2m-1) - \frac{4k_p[M]_0C_2}{k_d} e^{-(m+1)(Z_0-Z)} \times \sum^{2} (m) - \frac{2k_p[M]_0}{k_t(m-1)}\left(\frac{[M]}{[M]_0}\right) - \frac{2k_p[M]_0}{k_t} \times e^{-(m)(Z_0-Z)} \sum^{2} (m-1) - \frac{[M]_0}{1-\frac{1}{m}}\left(\frac{[M]}{[M]_0}\right) + C_2^*\left(\frac{[M]}{[M]_0}\right)^{1/m} \quad \text{(A1.16)}$$

$Q_2 = Q_{20}$ at $Z = Z_0$

$$\therefore C_2^* = Q_{20} - \frac{k_d}{2k_t}(Z_0+1) + \frac{2k_p[M]_0}{k_t(m-1)} + \frac{[M]_0}{1-\frac{1}{m}} \quad \text{(A1.17)}$$

The differential equation governing second moment of dead polymer distribution (eq. 50) is

$$\frac{d\lambda_2}{dt} = k_t[P]Q_2 + k_{tc}Q_1^2 + k_{tr}[S]Q_2$$

Integrating eq. (51), using eq. (A1.4) and eq. (30), we obtain upon substitution of the limits

$$\int k_{tc}Q_1^2 = \frac{2k_{tc}}{k_d}\Bigg[\left(\frac{k_d}{2k_t}\right)^2 \times \left\{\frac{1}{2}(Z_0^2 - Z^2) + 2(Z_0-Z) + ln(Z_0-Z)\right\} - C_1^2 e^{-2m(Z_0-Z)} \sum^{2} (2m) - C_2^2 e^{-2(Z_0-Z)} \sum^{2} + C_1 \times \left(\frac{k_d}{k_t}\right)\frac{1}{m}{}^{(1-e^{-m(Z_0-Z)})} - C_1\left(\frac{k_d}{k_t}\right) e^{-m(Z_0-Z)} \times \sum^{2} (m + C_2\left(\frac{k_d}{k_t}\right)(1-e^{-(Z_0-Z)}) - C_2\left(\frac{k_d}{k_t}\right) e^{-(Z_0-Z)} \sum^{2} (1)\Bigg] \quad \text{(A1.18)}$$

Further,

$$\int k_t[P]Q_2dt = -\frac{k_t}{k_p}\int \frac{Q_2}{\left(\frac{[M]}{[M]_0}\right)} d\left(\frac{[M]}{[M]_0}\right) = -\frac{k_t}{k_p}\int \frac{Q_2}{\frac{[M]}{[M]_0}} m\left(\frac{[M]}{[M]_0}\right) dZ = -\int Q_2dZ$$

Integrating eq. (A1.16), using eq. (A1.4), we get,

$$\int k_t[P]Q_2dt = \frac{k_d}{k_t}\left[\frac{1}{2}(Z_0^2 - Z^2) + 2(Z_0-Z)\right] - \frac{3[M]_0}{(m-1)}(1-e^{-m(Z_0-Z)}) + \frac{2k_p[M]_0}{k_t}$$

$$\times e^{-m(Z_0-Z)}) \sum^{3} (m-1, m) + \frac{4k_p[M]_0C_1}{k_d}$$

$$\times \sum^{3} (2m-1, 2m) + \frac{4k_p[M]_0C_2}{k_d} e^{-(m+1)(Z_0-Z)}$$

$$\times \sum^{3} (m, m+1) + C_2^*(1 - e^{-(Z_0-Z)}) \quad (\mathrm{A1.19})$$

Where C_2^* is as defined in eq. (A1.17), and

$$\sum^{3} (X, Y) = \sum_{n=0}^{\infty} \frac{1}{Z_0^{n+1}} \sum_{r=0}^{n} \frac{n!}{(n-r)!\, X^{r+1}}$$

$$\times \sum_{p=0}^{n-r} \frac{(n-r)!\,(Z_0-Z)^{n-r-p}}{(n-r-p)!\, Y^{p+1}} \quad (\mathrm{A1.20})$$

Therefore,

$$\lambda_2 - \lambda_{20} = \frac{2k_{tc}}{k_d}\Bigg[\left(\frac{k_d}{2k_t}\right)^2$$

$$\times \left\{\frac{1}{2}(Z_0^2 - Z^2) + 2(Z_0 - Z) + ln(Z_0 - Z)\right\}$$

$$- C_1^2 e^{-2m(Z_0-Z)} \sum^{2} (2m) - C_2^2 e^{-2(Z_0-Z)} \sum^{2} (2)$$

$$+ C_1\left(\frac{k_d}{2k_t}\right)\frac{1}{m}(1-e^{-m(Z_0-Z)}) - C_1\left(\frac{k_d}{k_t}\right)e^{-m(Z_0-Z)}$$

$$\times \sum{}^{2}(m) + C_2\left(\frac{k_d}{k_t}\right)(1-e^{-(Z_0-Z)})$$

$$- C_2\left(\frac{k_d}{k_t}\right)e^{-(Z_0-Z)} \sum{}^{2}(1)\Bigg] + \frac{k_d}{2k_t}$$

$$\times \left[\frac{1}{2}(Z_0^2 - Z^2) + 2(Z_0 - Z)\right]$$

$$- \frac{3[M]_0}{(m-1)}(1 - e^{-m(Z_0-Z)}) + \frac{4k_p[M]_0C_1}{k_d}$$

$$\times e^{-2m(Z_0-Z)} \sum^{3} (2m-1, 2m) - \frac{4k_p[M]_0C_2}{k_d}$$

$$\times e^{-(m+1(Z_0-Z)} \sum^{3} (m, m+1)$$

$$+ \frac{2k_p[M]_0 e^{-m(Z_0-Z)}}{k_t} \sum^{3} (m-1, m)$$

$$+ C_2^*(1 - e^{-(Z_0-Z)}) + \frac{k_{tr}[S]_0}{p_3k_t}(e^{p_3(Z_0-Z)} - 1)$$

$$+ \frac{k_{tr}[S]_0}{p_3Z_0k_t}(e^{p_3(Z_0-Z)} - 1)$$

$$- \frac{8[S]_0k_p[M]_0C_1}{(k_dZ_0)^2(2m-1)p_4}(e^{p_4(Z_0-Z)} - 1)$$

$$- \frac{8[S]_0k_p[M]_0C_2}{(k_dZ_0)^2 mp_5}(e^{p_5(Z_0-Z)} - 1)$$

$$- \frac{4[S]_0k_p[M]_0}{k_dZ_0^2k_t(m-1)p_1}(e^{p_1(Z_0-Z)} - 1)$$

$$- \frac{2[S]_0[M]_0}{k_dZ_0(1-1/m)p_1}(e^{p_1(Z_0-Z)} - 1)$$

$$+ \frac{2C^*[S]_0}{k_dZ_0p_2}(e^{p_2(Z_0-Z)} - 1) \quad (\mathrm{A1.21})$$

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