# Minimum end time policies in batch, chain addition polymerizations

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## INTRODUCTION

Production of polymers within minimum possible time without sacrificing the physical properties can be achieved by changing certain control variables in a 'systematic manner'. The control variables generally considered in the polymerization reactions are temperature and initial initiator concentration. Pontryagin's maximum principle[1] is an effective tool in deciding the optimum values of these control variables.

Ray *et al.*[2] applied the maximum principle for deciding the optimal control variables for a given monomer conversion and average molecular weight without considering gel effect. Later, Biesenberger *et al.*[3] considered the gel effect, but did not specify the optimal initial initiator concentration while deciding the optimum temperature/time cycle. Chen and Jeng[4] have filled this gap in the model and verified the model experimentally considering the system of styrene polymerization.

The polymerizations of methylmethacrylate and vinyl acetate are also generally done by batch process[5]. Hence, the minimum end time problem is studied for these systems for a wide range of number average chain lengths.

## KINETIC MECHANISM AND STATE EQUATIONS

Radical chain polymerization has generally been represented by the following mechanism[6].

Initiation:

$$I \xrightarrow{k_d} 2R \qquad R = 2fk_d I^n \tag{1}$$

$$R + M \xrightarrow{k_i} P_1 \tag{2}$$

Here, $f$ is the initiator efficiency.

Propagation:

$$P_x + M \xrightarrow{k_p} P_{x+1} \tag{3}$$

Termination:

$$P_x + P_y \xrightarrow{k_{td}} M_x + M_y \text{ (Disproportionation)} \tag{4}$$

$$P_x + P_y \xrightarrow{k_{tc}} M_{x+y} \text{ (Combination)} \tag{5}$$

Here, the chain transfer reaction is neglected and the kinetic constants are assumed to be independent of chain length.

In radical chain polymerization, there is an autocatalytic effect, which is termed the gel effect[6]. This effect is due to increased viscosity as monomer conversion increases and it retards the rate of termination. This effect is taken into account by the gel effect function[3] $g(m)$ which gives the relation between $k_t$ and monomer conversion ($m$).

$$k_t = k_{tc} + k_{td} = k_{to}(y)g^2(m) = A_t \exp(-E_t y)g^2(m) \tag{6}$$

where

$$\begin{aligned} g &= g(m) \quad \text{as } m > m_1 \quad \text{(with gel effect)} \\ &= 1 \quad \text{as } 0 \leqslant m \leqslant m_1 \quad \text{(without gel effect)} \end{aligned} \tag{7}$$

$m_1$ is the monomer conversion above which the gel effect becomes significant.

Adopting the method of moment generating functions[3], the equations for the 3 state variables namely, initiator conversion ($c$), dimensionless zeroth and first moments of the molecular weight distribution ($\xi_0$, $\xi_1$) can be written as

$$\frac{dm}{dt} = \frac{d\xi_1}{dt} = k_1(1-c)^{0.5n}\frac{(1-m)}{g} + 2ak_2(1-c)^n \tag{8}$$

$$\simeq k_1(1-c)^{0.5n}\frac{(1-m)}{g} \tag{9}$$

(by making long chain approximation)

$$\frac{dc}{dt} = k_2(1-c)^n \tag{10}$$

$$\frac{d\xi_0}{dt} = (2-v)ak_2(1-c)^n \tag{11}$$

with the initial conditions

$$m(0) = c(0) = \xi_0(0) = 0 \tag{12}$$

The number average chain length is given by

$$X_n = m/\xi_0 \tag{13}$$

## BEST ISOTHERMAL POLICY

Following a procedure similar to that adopted by Chen and Jeng[4] we get the following expressions for the control variables, $I_0$ and $T$, and for the end times, $t_f$, for the isothermal polymerization.

$$\frac{E_2}{2(E_2-E_1)}\ln\left(1-\frac{B}{\gamma I_0}\right) + \frac{B/\gamma I_0}{\left(1-\frac{B}{\gamma I_0}\right)^{0.5}} = 0 \tag{14}$$

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where

$$\gamma=\left(2-\frac{k_{tc}}{k_t}\right);\quad B=M_0m^*/fX_n^*$$

$$y=\frac{1}{R_gT}=\frac{1}{(E_2-E_1)}\ln\left[\frac{W}{2DI_0^{0.5}\left[1-\left(1-\frac{B}{\gamma I_0}\right)^{0.5}\right]}\right] \tag{15}$$

where

$$W=\int_0^m\frac{g}{1-m}\,\mathrm{d}m \tag{15a}$$

$$D=\frac{A_1}{A_2}(2f)^{0.5} \tag{15b}$$

and

$$t_f=-\frac{1}{A_2\exp(-E_2y)}\ln\left(1-\frac{B}{\gamma I_0}\right) \tag{16}$$

The initiator conversion ($c$) can be obtained by solving equation (14) for $B/\gamma I_0(=c(t_f))$ which is constant for a given polymer[4]. The value of the best $I_0$ is substituted in equation (15) to obtain the best temperature and then $t_f$ is calculated from equation (16).

## OPTIMAL TEMPERATURE POLICY

The maximum principle is applied to obtain the optimal temperature profile in a manner similar to that of Chen and Jeng[4]. According to the maximum principle the Hamiltonian, $H$, should be minimum if the objective function is to be minimum[7] and this minimum value is equal to zero if $t_f$ is not specified[1].

Objective function: $F=\{t_f\}$

$$H=1+\lambda_1k_1(1-c)^{0.5n}\frac{(1-m)}{g}+\lambda_2k_2(1-c)^n+\lambda_3(2-v)ak_2(1-c)^n \tag{17}$$

where $\lambda_1$, $\lambda_2$ and $\lambda_3$ are the adjoint variables which are given by

$$\frac{\mathrm{d}\lambda_1}{\mathrm{d}t}=-\frac{\partial H}{\partial m}=-\lambda_1k_1(1-c)^{0.5n}\frac{\mathrm{d}}{\mathrm{d}m}\left(\frac{1-m}{g}\right) \tag{18}$$

$$\frac{\mathrm{d}\lambda_2}{\mathrm{d}t}=-\frac{\partial H}{\partial c}=\frac{n}{1-c}\left[\lambda_1k_1\frac{(1-m)}{2g}(1-c)^{0.5n}+\lambda_2k_2(1-c)^n+\lambda_3(2-v)ak_2(1-c)^n\right] \tag{19}$$

$$\frac{\mathrm{d}\lambda_3}{\mathrm{d}t}=-\frac{\partial H}{\partial\xi_0}=0 \tag{20}$$

with the boundary conditions

$$\begin{gathered}\lambda_1\ \text{undefined}\\ \lambda_2(t_f)=0\\ \lambda_3\ \text{undefined}\end{gathered} \tag{21}$$

The boundary conditions on the state variables are:

$$\begin{gathered}m(0)=0\quad m(t_f)=m^*\\ c(0)=0\quad c(t_f)=\text{unknown}\\ \xi_0(0)=0\quad \xi_0(t_f)=m^*/X_n^*\end{gathered} \tag{22}$$

The following necessary conditions are obtained from the maximum principle.

$$H=0 \tag{23}$$

$$\frac{\partial H}{\partial y}=0 \tag{24}$$

$$\frac{\partial^2H}{\partial y^2}>0\quad\text{for } y=y_s \tag{25}$$

Thus, differentiating equation (17) with respect to $y$ and applying $H=0$, we get

$$\frac{\partial H}{\partial y}=(E_2-E_1)\lambda_1k_1(1-c)^{0.5n}\frac{(1-m)}{g}+E_2=0 \tag{26}$$

$$\frac{\partial^2H}{\partial y^2}=E_1E_2>0 \tag{27}$$

The solution of equation (26) gives the optimum temperature. Equation (26) contains one unknown, $\lambda_1$, which is obtained by integrating equation (18).

$$\lambda_1\frac{(1-m)}{g}=\text{constant}=L,\ \text{(for example)} \tag{28}$$

Substituting equation (28) in equation (26) and solving for $y$, we get

$$y_s=-\frac{1}{E_1}\ln\left[\frac{-E_2}{A_1(E_2-E_1)\lambda_1(1-c)^{0.5n}}\cdot\frac{g}{(1-m)}\right] \tag{29}$$

The following constraints on temperature could exist.

$$\begin{aligned}&\text{if}\quad T_s>\bar{T},\quad T=\bar{T}\\ &\text{if}\quad T_s<\underline{T},\quad T=\bar{T}\\ &\text{if}\quad \bar{T}\geqslant T_s\geqslant\underline{T},\quad T=T_s\end{aligned} \tag{30}$$

where $\bar{T}$ and $\underline{T}$ are the upper and lower limits on temperature.

### *Optimal initial initiator concentration* ($I_0$)

The application of maximum principle to fine optimum $I_0$ requires finding the expression for $\partial H/\partial I_0$. Thus,

$$\frac{\partial H}{\partial I_0} = \frac{n}{I_0}\left[-1-\frac{\partial H/\partial y - E_2}{2(E_2-E_1)}\right] \tag{31}$$

If the temperature is not constrained $\partial H/\partial y = 0$. Also, the value of $E_2/2(E_2-E_1)$ is observed to be greater than 1 for the systems under study, and hence, we get $\partial H/\partial I_0 > 0$, indicating that for the Hamiltonian to be minimum, $I_0$ should also be minimum. Hence, the optimum $I_0$ takes its lower limit $I_0$. However, if $I_0$ is decreased the conversion of the initiator increases approaching unity at a certain value of $I_0$. Thus the optimal $I_0$ is that which results in dead-end polymerization.

Even when the temperature is constrained, the contribution of the term $\partial H/\partial y$ will be small compared to that of $E_2$ and hence, we can come to the same conclusions.

## NUMERICAL CALCULATIONS

We will consider the following systems:

(1) Bulk polymerization of methylmethacrylate (MMA) initiated by 2,2-azoisobutyronitrile (AIBN).

(2) Bulk polymerization of vinyl acetate (VAC) initiated by AIBN.

The relevant data used for the two systems are given in *Table 1*. The following numerical procedures are adopted.

Best Isothermal Policy:

(1) Equation (14) is solved by Newton-Raphson search technique for obtaining the value of $c(t_f)$ and hence the best $I_0$.

(2) Equation (15a) is numerically integrated by 4th order Runge–Kutta algorithm to get the value of $W^*$.

(3) These values are substituted in equation (15) to get the best temperature.

Optimal Temperature Policy:

The procedure is similar to that adopted by Chen and Jeng[4]. 4th order Runge–Kutta algorithm is used to solve equations (9)–(11).

## RESULTS AND DISCUSSION

### *Best isothermal policy (BIP)*

The values of the control variables ($T$ and $I_0$) obtained from *BIP* are given in *Table 2* and also plotted in *Figure 1*. It can be observed from the Figure that there is a linear relationship between $X_n^*$ and $I_0$ and between $X_n^*$ and $t_f$ when plotted on a log–log scale. Lower values of $I_0$ are required for larger chain lengths whereas more reaction times are demanded. The temperature decreased with $X_n^*$. Thus if a polymer product of higher chain length is required, the reaction temperature should be lower and the reaction time should be more.

### *Optimal temperature policy (OTP)*

*Figure 2* gives the optimal temperature profiles for methylmethacrylate system for $X_n^* = 5000$ for various values of $I_0$. It can be seen that the temperature rise with respect to time should be more as the $I_0$ value is decreased. At larger values of $I_0$, the optimal temperature should be maintained as nearly constant. As $I_0$ is decreased the slope of the optimum temperature profile is increasing at a slower rate in the initial part of the profile and at a higher rate in the latter part of the profile. The profile labeled 1 is the optimum temperature profile at $I_{0a}$, the optimum value of $I_0$. The curve labelled 2 is the optimum temperature profile at $I_{0b}$, the best value of $I_0$ which is obtained from BIP. $I_{0b}$ is not the optimum $I_0$ and the $I_{0b}$ is less than the $I_{0a}$. It can be observed from *Figure 3* that as $I_0$ is decreased, the time

*Table 1* Kinetic data of MMA and VAC

| | Methylmethacrylate[3] | Vinyl acetate[5,8,9] |
|---|---|---|
| $A_p$, l s$^{-1}$ mol$^{-1}$ | 5.1 x 10$^6$ | 3.2 x 10$^7$ |
| $A_t$, l s$^{-1}$ mol$^{-1}$ | 7.8 x 10$^8$ | 3.7 x 10$^9$ |
| $A_d$, l s$^{-1}$ mol$^{-1}$ | 1.58 x 10$^{15}$ | 7.9 x 10$^{16}$ |
| $E_p$, cal mol$^{-1}$ K$^{-1}$ | 6300 | 3130 |
| $E_t$, cal mol$^{-1}$ K$^{-1}$ | 2800 | 1460 |
| $E_d$, cal mol$^{-1}$ K$^{-1}$ | 30800 | 34000 |
| $v$ | 0.0 | 0.0 |
| $f$ | 0.6 | 0.6 |
| $g(m)$ | 1.0 for $0 \leqslant m \leqslant 0.15$<br>$\dfrac{1}{(1-28.72m+228.2m^2-239.9m^3)}$ for $0.15 < m \leqslant 0.6$ | $\dfrac{1}{(1+1.767m+1.34m^2-3.58m^3)}$ for $0 \leqslant m \leqslant 0.5$ |

*Table 2* Comparison of best isothermal policy (BIP) and optimal temperature policy (OTP)

| | | End time, $t_f$ | | | | | Initial initiator concentration, $I_0$ | | Temperature range | |
|---|---|---|---|---|---|---|---|---|---|---|
| System | $X_n$* | BIP (s) | OTP (s) | % reduction | $t_f$* (s) | % reduction | BIP g mol$^{-1}$ | OTP g mol$^{-1}$ | BIP (K) | OTP (K) |
| MMA | 2000 | 327 | 260 | 20.5 | 278 | 15.0 | 0.203 x 10$^{-2}$ | 0.195 x 10$^{-2}$ | 388.5 | 382.1–423.6 |
| | 5000 | 1254 | 974 | 22.3 | 1084 | 13.6 | 0.813 x 10$^{-3}$ | 0.780 x 10$^{-3}$ | 375.8 | 370.1–418.5 |
| | 10000 | 3465 | 2680 | 22.7 | 2975 | 14.1 | 0.407 x 10$^{-3}$ | 0.390 x 10$^{-3}$ | 366.7 | 361.3–411.0 |
| | 20000 | 9577 | 7490 | 21.8 | 8270 | 13.6 | 0.203 x 10$^{-3}$ | 0.195 x 10$^{-3}$ | 358.0 | 352.8–393.3 |
| | 50000 | 36719 | 28500 | 22.4 | 31800 | 13.4 | 0.813 x 10$^{-4}$ | 0.780 x 10$^{-4}$ | 347.1 | 342.3–384.7 |
| VAC | 1.0 x 10$^7$ | 965 | 840 | 13.0 | 904 | 6.3 | 0.526 x 10$^{-6}$ | 0.455 x 10$^{-6}$ | 376.8 | 373.4–410.5 |
| | 2.0 x 10$^7$ | 2163 | 1880 | 13.1 | 2030 | 7.1 | 0.263 x 10$^{-6}$ | 0.227 x 10$^{-6}$ | 370.2 | 367.0–405.2 |

$t_f$*: End time, $t_f$, in optimal policy at best $I_0$ which is obtained from BIP

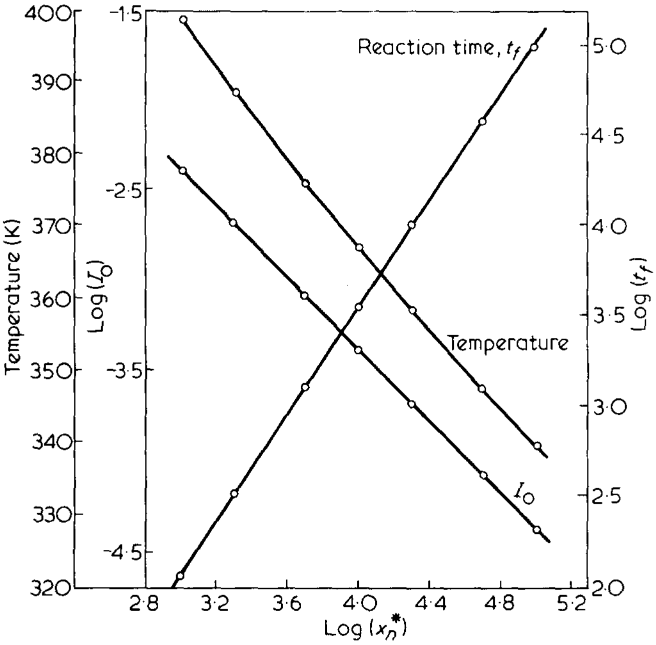

*Figure 1* Dependence of temperature ($T$), initial initiator concentration ($I_0$) and reaction end time ($t_f$) on number average chain length ($X_n^*$) in best isothermal policy

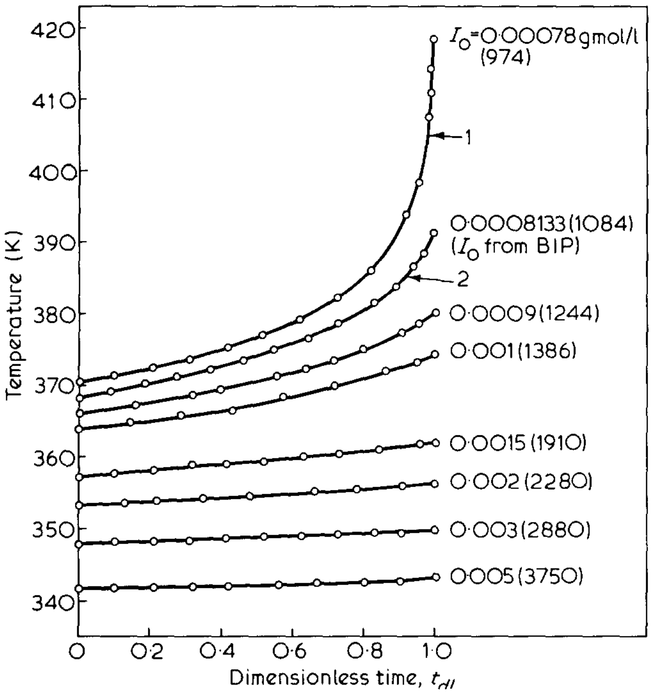

*Figure 2* Temperature profiles at various values of $I_0$ for $X_n^*$ = 5000. System: methylmethacrylate, figures in parentheses are $t_f$ in seconds

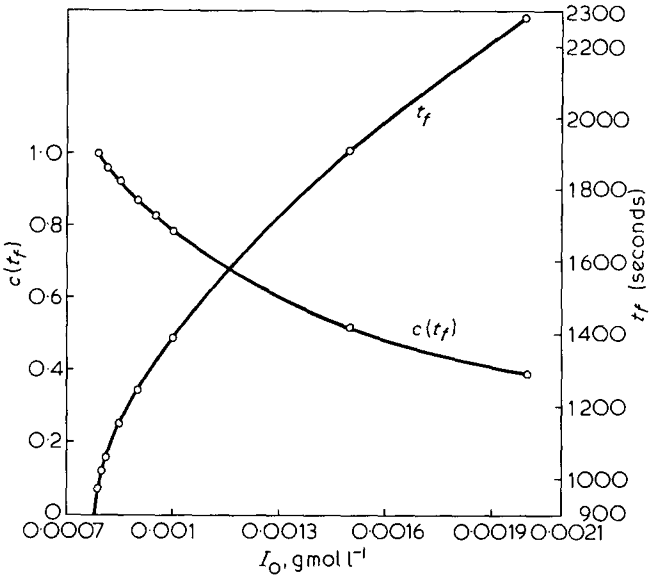

*Figure 3* Dependence of $t_f$ and $c(t_f)$ on $I_0$ using optimal temperature policies for $X_n^*$ = 5000. System: methylmethacrylate

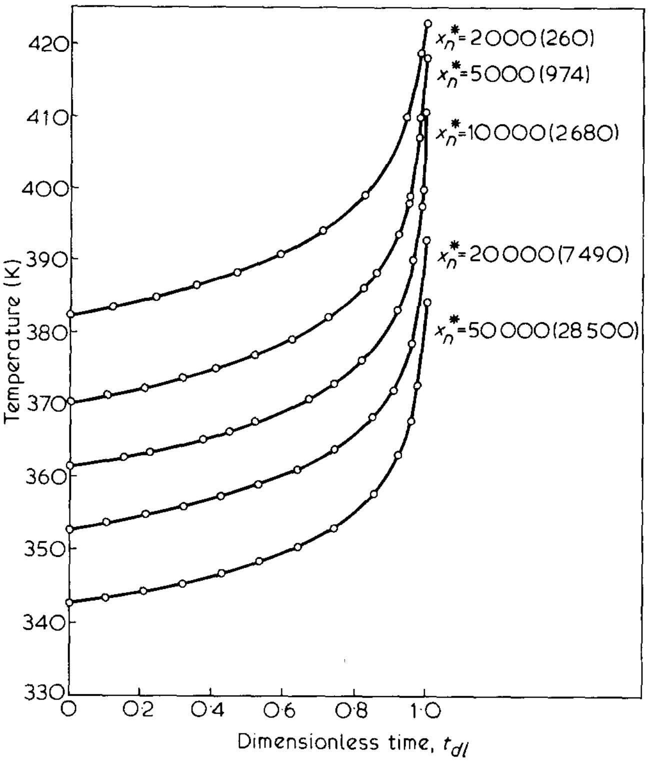

*Figure 4* Optimal temperature profiles for various values of $X_n^*$. System: methylmethacrylate, figures in parentheses are $t_f$ in seconds

($t_f$) is decreasing whereas the initiator conversion $c(t_f)$ is increasing, the latter approaching finally to a value unity at a value of $I_0 = 7.8 \times 10^{-4}$ below which there is no possibility of attaining the required properties. This is the point of dead-end polymerization. Similar profiles and similar conclusions are observed for all $X_n^*$'s under study. *Figure 4* gives the optimum temperature profiles at optimum $I_0$ for various values of $X_n^*$. It can be seen that for larger chain lengths, lower operating temperatures are required.

The temperature profiles and the variation of the $t_f$ and $c(t_f)$ with $I_0$ for the vinyl acetate system are observed to be similar to the MMA system. The final optimum results for the VAC system are included in *Table 2*.

### *Comparison of the two policies*

It can be seen from *Table 2* that there is considerable reduction in $t_f$ when optimal policy is adopted. The reduction is in the range of 20–23% for MMA system, whereas for VAC system it is 13–14%. It can also be observed that even the optimal temperature policy at $I_{0b}$

gives 13–15% reduction in $t_f$ for the MMA system and 6–7% reduction for VAC system. Regarding the initial initiator concentration ($I_0$), lower values of $I_0$ are required by OTP then by BIP. However, both the values are nearly same.

*Comparison of the two systems MMA and VAC*

From the above discussion, it can be noted that the OTP gives better results for MMA than for VAC. Kinetics is going to play an important role in this respect. However, the chain transfer reaction which is not considered in the present study is more pronounced in the VAC system than in the MMA system.

## CONCLUSIONS

(1a) In the case of best isothermal policy (BIP), the number average chain length ($X_n^*$) and initial initiator concentration ($I_0$) follow linear relationship on a log–log plot. Similar relation exists between $X_n^*$ and $t_f$.

(1b) For larger chain lengths lower values of temperature and $I_0$ are required.

(2) When compared to BIP, the optimal temperature policy makes it possible to get more than 20% reduction in reaction time in the case of MMA system and about 13% reduction in the case of VAC system.

(3) The optimum temperature policies for both the systems are of increasing temperatures with the lowest possible values of initial initiator concentration, $I_{0u}$.

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## GLOSSARY

| | |
|---|---|
| $a$ | $fI_0^n/M_0$ |
| $A_d,A_p,A_t$ | frequency factor for initiator decomposition, propagation and termination, respectively |
| $B$ | $M_0m^*/fX_n^*$ |
| $c$ | initiator conversion $(\mathrm{I}-I/I_0)$ |
| $E_d,E_p,E_t$ | activation energies for initiator decomposition, propagation and termination, respectively |
| $f$ | initiator efficiency |
| $g$ | gel effect function $g(m)=(k_t/k_{t0})^{0.5}$ |
| $H$ | Hamiltonian defined by equation (17) |
| $I$ | initiator concentration |
| $I_0$ | initial initiator concentration |
| $\underline{I_0}$ | lower limit of $I_0$ |
| $k_1,k_2$ | lumped kinetic parameters, corresponding frequency factors being $A_1,A_2$ and energies of activation $E_1,E_2$ respectively |
| $k_d,k_i,k_p$ | kinetic constants for initiator decomposition, initiation and propagation, respectively |
| $k_{tc},k_{td}$ | kinetic constants for termination by combination and disproportionation, respectively |
| $k_t$ | $k_{tc}+k_{td}=k_{t0}(y).g^2(m)$ |
| $m$ | monomer conversion |
| $m_1$ | the monomer conversion from which the gel effect becomes significant |
| $m^*$ | target monomer conversion |
| $M_0$ | initial monomer concentration |
| $M$ | monomer concentration |
| $M_x,M_y,M_{x+y}$ | concentration of dead polymer of chain lengths $x$, $y$, and $x+y$, respectively |
| $P_x,P_y$ | concentration of growing polymer of chain length $x,y$, respectively |
| $R$ | concentration of primary radicals |
| $R_g$ | gas constant |
| $t$ | time |
| $t_{dl}$ | dimensionless time, $t/t_f$ |
| $t_f$ | reaction end time |
| $T$ | absolute temperature |
| $\underline{T},\bar{T}$ | lower and upper bounds on temperature |
| $T_s$ | optimum temperature |
| $v$ | $k_{tc}/k_t$ |
| $X_n$ | number average chain length |
| $X_n^*$ | target number average chain length |
| $y$ | $1/R_gT$ |
| $\underline{y}$ | the limit of $y$, corresponding to the lower bound of the temperature, $\underline{T}$ |
| $\bar{y}$ | the limit of $y$, corresponding to the upper bound of the temperature, $\bar{T}$ |
| $y_s$ | stationary temperature policy. Solution to $\partial H/\partial y=0$ |

*Greek symbols*:

| | |
|---|---|
| $\gamma$ | $2-v$ |
| $\lambda_i$ | adjoint variable |
| $\xi_i$ | dimensionless $i$th moment of the dead polymer molecular weight distribution |