

Non-isothermal Modelling of Solution Polymerization of Methyl Methacrylate for Control Purposes

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ABSTRACT

A mathematical model is developed for the solution polymerization of methyl methacrylate (MMA) in a batch reactor. The model includes the whole process. In polymerization part, model includes chain transfer and termination by both combination and disproportionation. Variation in reactant mixture properties is included in the model. The glass and gel effects are included by CCS (Chiu, Carratt and Soong) model. Energy balances are applied to the reactor, oil bath, and temperature sensors. Therefore, the model can attribute to the non-isothermal process. The final model consists of fourteen nonlinear stiff differential equations. Output of the model is monomer conversion, initiation concentration, radical concentration, dead polymer concentration, volume, and reactor and jacket temperatures. Agreement of model prediction and experimental results is very good. This model can be used for optimization and control studies because it includes the whole process.

Key Words: methyl methacrylate, solution polymerization, modelling, non-isothermal and free radical

INTRODUCTION

During the polymerization process, some small molecules, called monomer, react to form long polymer chain. To reach specific polymer with certain properties one needs enough recognition of polymerization mechanism and process conditions. The recognition of the polymerization plays a key role in polymer engineering. In this way, process modelling is an essential tool for a better understanding of the relationship among various variables. Kinetic studies are usually complex because of cage effect, gel phenomena, and

glass effect that make the process highly nonlinear. Hence, an acceptable model should take into consideration these important aspects of the free radical polymerization.

Last decade has witnessed a considerable increase in the understanding of various aspects of the complex chain polymerization systems. Louie et al. [1] reviewed gel effect models and their theoretical foundation. Then, they extended a previously developed bulk polymerization model for the solution polymerization of methyl methacrylate. They validated their model for a range of experimental conditions. Kapoor et al. [2]

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took into account changes in the physical property of the reaction mass during the course of the reaction. Then, using the nonlinear ordinary differential equations (NLDE) model, they computed the sensitivity of the temperature maximum in a plug tubular reactor (mathematically, batch polymerization model is equivalent to a plug tubular reactor model).

For polymethyl methacrylate, they showed that gel effect takes place in the temperature maximum. They suggested that the dimensionless propagation activation energy and the dimensionless initiation activation energy are the most important parameters governing the system performance. Kumar and Gupta [3] proposed several different correlation for methyl methacrylate polymerization for the parameters θ_p , θ_i , and A characterizing the gel and glass effects in the model CCS (Chui, Carratt and Soong) [20]. They used an optimal parameter estimation technique to obtain new correlation. Therefore, the agreement between calculation and experiment improved.

However, they included some undesired rigorous mathematical methods in the model. Later, Vaid and Gupta [4] used their examined kinetic model to obtain an optimal temperature history for methyl methacrylate. They put end point constraints, monomer conversion, and number average chain length for the process. Their algorithm was based on the Pontryagin's minimum principle and lagrangian multipliers. Although, their method was more efficient, they did not support their theoretical results by experiment. Butala et al. [5] improved the batch polymerization of styrene using optimal initiator mixture and temperature. They illustrated through kinetic model simulation and experiments. Penlidis et al. [6] presented a tutorial article and gave a general background section on mathematical modeling.

Then, they derived a mechanistic model for free radical polymerization of methyl methacrylate. Subsequently, they showed how this complex model could be simplified. They discussed five models of different level of complexity for process optimization and control application. However, they did not apply any of these models for controller design and did not carry out any control studies. Ray et al. [7, 8] developed a new model to account for the gel and glass

effects under batch and semibatch reactor conditions. They used the free volume theory of Vrentas and Duda to account for the changes in the diffusion coefficients. They tuned the model parameters using experimental data on the isothermal methyl methacrylate. Their outcome was well suited with experimental results. Scall et al. [9] presented a method to determine an optimal temperature profile that guaranteed having controlled molecular weight distribution and desired molecular weight.

On the basis of the kinetic model, they determined the temperature profile by imposing the value of the instantaneous chain length to be maintained constant. In addition, they used few simplifying assumptions. They did not use any specific controller to track the optimal temperature trajectory. Tefera et al. [10, 11] developed a systematic method for the selection of model for the high conversion free radical polymerization exhibiting the gel and glass effects. They used the polymerization of MMA with AIBN system for demonstration purposes. They carried out their experiments isothermally. Then, they suggested a semi-empirical model to describe the conversion, polymerization degree, and molecular weight distribution for the entire course of the reaction. Ahn et al. [12] used Pontryagin's minimum principle to calculate an optimal temperature trajectory using the kinetic model for a batch polymerization reactor. Their experiments show that their trajectory is effective.

Some researchers have studied the control of polymerization reactor for the last three decades [13–18]. Usually, they preferred to use an experimental model for the polymerization and focused on the control studies part. For process engineer, it is more desirable to relate controller parameters to the process parameters and variables. Soroush and Karavaris [19] used a simple kinetic based model and designed a globally linearizing control for a batch polymerization reactor. Their model includes only monomer concentration, initiator concentration, reactor and jacket temperatures. However, there are more variables. Their controller performance is better than a PID controller tuned by try and error.

In sight of the above literature review, it is clear that a suitable model for the polymerization process

Table 1. Mechanism of free radical polymerization.

Polymerization stage	Polymerization mechanism	
Initiation	$I \xrightarrow{k_d} 2R^\circ + G$	$R_d = k_d[I]$
	$R^\circ + M \xrightarrow{k_{d1}} P_1^\circ$	$R_{i1} = k_{d1}[R^\circ][M]$
	$2R^\circ \xrightarrow{k_{i2}} I'$	$R_{i2} = k_{i2}[R^\circ]^2$
Propagation	$P_n^\circ + M \xrightarrow{k_p} P_{n+1}^\circ$	$R_p = k_p[M][P_n^\circ]$
Termination	$P_n^\circ + P_m^\circ \xrightarrow{k_{tc}} D_{n+m}$	$R_{tc} = k_{tc}[P_n^\circ][P_m^\circ]$
	$P_n^\circ + P_m^\circ \xrightarrow{k_{td}} D_n + D_m$	$R_{td} = k_{td}[P_n^\circ][P_m^\circ]$
Transfer	$P_n^\circ + M \xrightarrow{k_{tf}} P_1^\circ + D_n$	$R_{tf} = k_{tf}[M][P_n^\circ]$
	$P_n^\circ + M \xrightarrow{k_{ts}} S^\circ + D_n$	$R_s = k_{ts}[M][P_n^\circ]$

for control purposes should cover the whole process. Whole process means every part between the manipulated variables and controlled variables. In this paper, a non-isothermal model is proposed for solution polymerization of methyl methacrylate. The whole process including heating oil bath, electrical heaters, and cooling water coil is included in the model. This model is suitable for control studies.

Polymerization Mechanism

Methyl methacrylate normally is produced by a free radical, chain addition polymerization. Free radical polymerization consists of three main reactions: initiation, propagation and termination. Free radicals are formed by the decomposition of initiators. Once formed, these radicals propagate by reacting with surrounding monomers to produce long polymer chains; the active site being shifted to the end of the chain when a new monomer is added. During the propagation, millions of monomers are added to P_1° radicals. During termination, due to reactions among free radicals, the concentration of radicals decreases. Termination is by combination or disproportionation reactions. For methyl methacrylate, above 70 °C disproportionation is significant and below 40 °C combination reaction is dominant. At a time, there are minor quantities of radicals; the propagation step takes place more than the termination step. With chain transfer reactions to monomer, initiator, solvent, or even polymer, the active free radicals are converted

to dead polymer [1]. Table 1 gives the basic free radical polymerization mechanism.

The free radical polymerization rate decreases due to reduction of monomer and initiator concentration. However, due to viscosity increase beyond a certain conversion there is a sudden increase in the polymerization rate because. This effect is called Trommsdorff, gel, or auto-acceleration effect. For bulk polymerization of methyl methacrylate beyond the 20% conversion, reaction rate and molecular weight suddenly increase. In high conversion, because of viscosity increase there is a reduction in termination reaction rate.

EXPERIMENTAL

A schematic representation of the experimental batch reactor setup, used in this work, is shown in Figure 1. The reactor is a one-liter Buchi type jacketed, cylindrical glass vessel. Its inside diameter is 100 mm while its height is 127 mm. The reactant mixture is agitated by a multipaddle agitator, which is driven by a three-phase motor mounted on the reactor. The speed of the stirrer is kept constant throughout the course of the polymerization process.

The computer is a Pentium II 500 Hz that is connected to the reactor via an ADCPWM-01 analog/digital I/O data acquisition card. The analog signals from the measuring elements are converted to

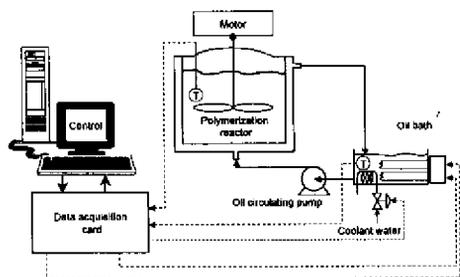


Figure 1. Schematic experimental system.

voltage and amplified to 0–5 volts (which is card input). The data acquisition software is developed internally in this department.

The necessary heat transfer for heating or cooling of the reactant mixture is continuously supplied through the jacket of the reactor. The oil, which is heated in the bath, is circulated by a gear pump. The pump flow rate is 15 L/min. The heating/cooling system of the oil consists of two 1500 W electrical heaters and one coolant water coil, which is operated by a on/off Acco brand electrical valve. Two temperature sensors, resistance temperature detectors (RTD), are used with accuracy $\pm 0.2^\circ\text{C}$.

In this system, input power to the heaters and heat transfer with coolant water in the coil are the manipulated variables. Intermediate electronic circuits

for connection of temperature sensors, heaters, and valve are made internally for control purposes.

Methyl methacrylate and toluene are used as monomer and solvent, respectively, in polymerization. Benzoyl peroxide (BPO) is used as the initiator. Produced polymer molecular weight is measured by Ubbelohde viscometer.

MATHEMATICAL MODELLING

In a batch reactor, all reactants are added in the beginning of the process. In order to calculate the concentration of different species, component mass balances should be written. Table 2 gives the component mass balance of the batch reactor. In this model, long chain approximation is used. Although, quasi steady state approximation (QSSA) is normally used for simplification, but in this model this assumption is used only in the beginning of the reaction to reach initial condition for the calculation of moments. Table 2 gives the infinite numbers of ordinary differential equations from the definition of moments; number of equations can be reduced to finite numbers of equations.

Definitions of moments are:

$$\lambda_k = \sum_{n=1}^{\infty} n^k [P_n^*], \quad \mu_k = \sum_{n=1}^{\infty} n^k [D_n] \quad (1)$$

Table 2. Component mass balance in a batch reactor.

$\frac{1}{V} \frac{d([M]V)}{dt} = -2fk_d[I] - (k_p + k_t)[M] \sum_{n=1}^{\infty} P_n^*$	
$\frac{1}{V} \frac{d([I]V)}{dt} = -k_d[I]$	
$\frac{1}{V} \frac{d([S]V)}{dt} = -k_s[S] \sum_{n=1}^{\infty} P_n^*$	
$\frac{1}{V} \frac{d([P_1^*]V)}{dt} = 2fk_d[I] - k_p[M][P_1^*] - k_t[P_1^*] \sum_{n=1}^{\infty} P_n^* + k_t[M] \sum_{n=1}^{\infty} P_n^* + k_s[S] \sum_{n=1}^{\infty} P_n^*$	
$\frac{1}{V} \frac{d([P_n^*]V)}{dt} = k_p[M]([P_{n-1}^*] - [P_n^*]) - k_t[P_n^*] \sum_{m=1}^{\infty} P_m^* - k_t[M][P_n^*] - k_s[S][P_n^*]$	$n \geq 2$
$\frac{1}{V} \frac{d([D_n]V)}{dt} = k_{td}[P_n^*] \sum_{n=1}^{\infty} P_n^* + \frac{1}{2} k_{tc} \sum_{m=1}^{n-1} [P_{n-m}^*][P_m^*] + k_r[M][P_n^*] + k_s[S][P_n^*]$	$n \geq 1$

Which λ_k and μ_k are alive and dead polymer chains?

k^{th} moments, respectively? Therefore, $\lambda_0 = \sum_{n=1}^{\infty} [P_n^*]$ is

the total concentration of radicals, $\mu_0 = \sum_{n=1}^{\infty} [D_n]$ is total

concentration of dead polymer, and $\lambda_1 + \mu_1$ is total number of monomer moles reacted.

The polymer production in this reaction is accomplished with contraction in the mixture volume. The volume contraction factor is:

$$\varepsilon = \frac{\rho_p - \rho_m}{\rho_p} \quad (2)$$

where, ρ_p is polymer density and ρ_m is monomer density. Assuming no volume change on mixing, V , instantaneous volume of the mixture can be written as:

$$V = V_m + V_s + V_p = \frac{M_0(1-x)}{\rho_m} + \frac{M_0x}{\rho_p} + \frac{M_s}{\rho_s} \quad (3)$$

where M_0 is the initial charge of monomer, M_s is the mass of solvent, V_m is the volume of monomer, V_p is the volume of polymer, V_s is the volume of solvent, x is monomer conversion and ρ_s is polymer density. Rearrangement of eqn (3) gives:

$$V = \frac{M_0}{\rho_m} [1 - (1 - \frac{\rho_m}{\rho_p})x] + \frac{f_s}{1-f_s} \frac{\rho_m}{\rho_{m0}} \frac{\rho_{s0}}{\rho_s} \quad (4)$$

where f_s is the initial volume fraction of solvent. Densities are function of temperature; over the wide range of temperature $\rho_m/\rho_{m0} \times \rho_{s0}/\rho_s$ is close to 1.0. Hence, the instantaneous volume of reactant mixture is:

$$V = \frac{M_0}{\rho_m} (1 - \varepsilon x + \beta) \quad (5)$$

β is defined as:

$$\beta = \frac{f_s}{1-f_s} \quad (6)$$

In isothermal case, the instantaneous volume of reactant mixture will be:

$$V = \frac{V_0}{1+\beta} (1 - \varepsilon x + \beta) \quad (7)$$

Monomer concentration is given by:

$$[M] = \frac{1}{V} [M]_0 V_0 (1-x) \quad (8)$$

These equations could be converted to the set of eqns (9)–(20) as mass governing equations of a batch free radical polymerization reactor.

$$\frac{dx}{dt} = \frac{2fk_d}{[M]_0 V_0} [I] + (k_p + k_t)(1-x)\lambda_0 \quad (9)$$

$$\frac{d[I]}{dt} = -k_d[I] - \frac{[I]}{V} \frac{dV}{dt} \quad (10)$$

$$\frac{d[S]}{dt} = -k_s[S]\lambda_0 - \frac{[S]}{V} \frac{dV}{dt} \quad (11)$$

$$\frac{d\lambda_i}{dt} = R_{\lambda_i} - \frac{\lambda_i}{V} \frac{dV}{dt} \quad i = 0,1,2 \quad (12)$$

$$\frac{d\mu_i}{dt} = R_{\mu_i} - \frac{\mu_i}{V} \frac{dV}{dt} \quad i = 0,1,2 \quad (13)$$

$$\frac{dV}{dt} = -\frac{M_0}{\rho_m} \left[\varepsilon \frac{dx}{dt} + x \frac{d\varepsilon}{dt} \right] \quad (14)$$

$$R_{\lambda_0} = 2fk_d[I] - k_t\lambda_0^2 \quad (15)$$

$$R_{\lambda_1} = 2fk_d[I] - k_t\lambda_0\lambda_1 + (k_s[S] + k_t[M])(\lambda_0 - \lambda_1) + k_p[M]\lambda_0 \quad (16)$$

$$R_{\lambda_2} = 2fk_d[I] - k_t\lambda_0\lambda_2 + k_s[S](\lambda_0 - \lambda_2) + k_p[M](2\lambda_1 + \lambda_0) + k_t[M](\lambda_0 - \lambda_2) \quad (17)$$

$$R_{\mu_0} = (k_{td} + \frac{1}{2}k_{tc})\lambda_0^2 + (k_f[M] + k_s[S])\lambda_0 \quad (18)$$

$$R_{\mu_1} = k_t\lambda_0\lambda_1 + (k_f[M] + k_s[S])\lambda_1 \quad (19)$$

$$R_{\mu_2} = k_t \lambda_0 \lambda_2 + k_{tc} \lambda_1^2 + (k_f [M] + k_s [S]) \lambda_2 \quad (20)$$

Modelling of Diffusion Phenomena

During the free radical polymerization, three diffusion effects occur: cage, glass, and gel effects. There are different methods to model these effects. For the sake of brevity, the selected models are presented.

Interested readers may find some review in the literature [11]. For the cage effect, the rate of initiation is simplified by incorporating primary radical termination with an initiator efficiency factor:

$$2f k_d [I] = 2k_d [I] - k_{ti} [R^\cdot]^2 \quad (21)$$

There are different methodologies in order to take into consideration the glass and gel effects. Tefera et al. [10] summarized the most important models such as viscosity, reptation theory, entanglement concept and free volume theory. They mentioned that this classification is not definite due to their hybrid modelling backgrounds. In this study, glass and gel effects are modelled according to CCS model, which is suggested by Chiu et al. [20]. The CCS model basically is based on the free volume theory. In the CCS model, diffusion is incorporated as an integrated part of the propagation and termination from the beginning until the end of the polymerization. This eliminates the need for the use of a critical break point, the sudden introduction of diffusion effects, and the associated segmentation of model in different parts. Therefore, propagation rate constant, k_p , is variable:

$$\frac{1}{k_p} = \frac{1}{k_{p0}} + \theta_p \frac{\lambda_0}{D} \quad (22)$$

k_{p0} is changing as Arrhenius function, and D is:

$$D = \exp\left[\frac{1 - \varphi_p}{A + B(1 - \varphi_p)}\right] \quad (23)$$

θ_p is adjustable parameter:

$$\theta_p = 5.4814 \times 10^{-14} \exp\left(-\frac{13982}{T}\right) \quad (24)$$

Similarly, termination rate constant, k_t , is:

$$\frac{1}{k_t} = \frac{1}{k_{t0}} + \theta_t \frac{\lambda_0}{D} \quad (25)$$

k_{t0} is changing as Arrhenius function. θ_t is adjustable parameter:

$$\theta_t = \frac{2.2706 \times 10^{-23}}{[I]_0} \exp\left(\frac{17420}{T}\right) \quad (26)$$

$[I]_0$ is initial concentration of initiator. Table 3 gives parameters of the CCS model. All the other necessary parameters and constants for this model are given in the Table 4.

There are different approaches for molecular weights and their distribution. Usually, the exact distribution is not necessary. Hence, in this study, Number average molecular weight \bar{M}_n , weight average molecular weight \bar{M}_w , and polydispersity index are calculated by moments:

$$\bar{M}_n = M_m \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0}, \quad \bar{M}_w = M_m \frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1} \text{ and}$$

Table 3. Glass and gel effects parameters in CCS model.

$$\frac{k_t}{k_t^0} = \frac{D}{D + \theta_p k_t \lambda_0}, \quad \frac{k_p}{k_p^0} = \frac{D}{D + \theta_p k_p \lambda_0}$$

$$D = \exp\left[\frac{(1 - \varphi_p)}{A + B(1 - \varphi_p)}\right], \quad A = 0.168 - 8.21/10^{-6}(T_c - 114)^2, \quad B = 0.03^{\text{f}}$$

$$\theta_p = 5.4814 \times 10^{-14} \exp(13982/Tk), \quad \theta_t = \frac{2.2706 \times 10^{-23}}{[I]_0} \exp(17420/Tk)$$

$$[I]_0 = \left[\frac{\text{mol}}{l}\right], \quad \varphi_p = \frac{x(1 - \varepsilon)}{1 - \varepsilon x + \beta}$$

Table 4. Physical properties and rate constants [1].

$$\begin{aligned}
 f &= 1.0 \quad \text{for BPO, } \varepsilon = (\rho_p - \rho_m)/\rho_p, \rho_m [\text{g/mL}] = 0.968 - 1.225 \times 10^{-3} T^\circ\text{C} \\
 \rho_p &= 1.2 \quad \text{g/cm}^3, \rho_s = 0.883 - 9 \times 10^{-4} T^\circ\text{C g/mL}, \rho = \rho_m \phi_m + \rho_p \phi_p + \rho_s \phi_s \\
 \varepsilon &= \frac{\rho_p - \rho_m}{\rho_p} = 0.193 + 1.02 \times 10^{-3} T^\circ\text{C} \\
 \phi_m &= \frac{1-x}{1-\varepsilon x + \beta}, -\Delta H_p = 13900 \quad \text{cal/mol}, \phi_p = \frac{x(1-\varepsilon)}{1-\varepsilon x + \beta}, \phi_s = \frac{\beta}{1-\varepsilon x + \beta} \\
 C_{pm} &= C_{pp} = 1650 \text{ J/kg}^\circ\text{C}, C_{ps} = 1950 \text{ J/kg}^\circ\text{C}, C_p = C_{pm}\phi_m + C_{pp}\phi_p + C_{ps}\phi_s \\
 k_d &= 1.014 \times 10^{16} \exp\left(\frac{-30 \text{ kcal/mol}}{RT^\circ\text{K}}\right) \\
 k_{p0} &= 2.95 \times 10^7 \exp\left(\frac{-4.35 \text{ kcal/mol}}{RT^\circ\text{K}}\right) \\
 k_t &= 9.48 \times 10^3 \exp\left(\frac{-13.88 \text{ kcal/mol}}{RT^\circ\text{K}}\right) \times k_p \\
 k_s &= 1.01 \times 10^3 \exp\left(\frac{-11.40 \text{ kcal/mol}}{RT^\circ\text{K}}\right) \times k_p \\
 k_{t0} &= 5.88 \times 10^9 \exp\left(\frac{-0.701 \text{ kcal/mol}}{RT^\circ\text{K}}\right)
 \end{aligned}$$

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} \quad (27)$$

Energy Balances

Exothermic nature of the free radical polymerization is one of the most difficult features. Generated energy during polymerization should be removed by a coolant or dissipated to the environment. Otherwise, the reactor can thermally run away when the energy feeds back to increase temperature and reaction rates. Even if run away does not occur, molecular weight can be broadened. To model non-isothermal polymerization, energy balances should be taken into account. For present set up, energy balance should be applied to the reactant mixture in the reactor and oil in the bath. The following shows the application of energy balance to the reactant mixture:

$$mC_p \frac{dT}{dt} = (-\Delta H_p)k_p[M][\lambda_0]V - UA|_r(T - T_j) -$$

$$UA|_e(T - T_\infty) \quad (28)$$

where, m is the reactant mixture mass, C_p is the reactant mixture specific heat, $-\Delta H_p$ is the heat of polymerization, T is the reactant mixture temperature, T_j is the oil temperature, T_∞ is the environmental temperature, $UA|_r$ is the overall heat transfer coefficient between the reactant mixture and the jacket, and $UA|_e$ is the overall heat transfer coefficient between the reactant mixture and the environment. Energy balance of oil bath is [19]:

$$m_o C_{p_o} \frac{dT_j}{dt} = \alpha P + \alpha P - UA|_r(T_j - T) -$$

$$UA|_{o\infty}(T_j - T_{\infty}) - UA|_c(T_j - T_w) \quad (29)$$

which m_o is the oil mass, C_{po} is the specific heat of oil, T_w is the coolant water temperature, $UA|_{o\infty}$ is the overall heat transfer coefficient between the oil and environment, $UA|_c$ is the overall heat transfer coefficient between oil and coolant water, and α is the heat transfer coefficient between the heater and oil. These heat transfer coefficients could be calculated by empirical equations [21], but it needs a lot of information. In this study, these coefficients are estimated experimentally. Appendix A explains how to estimate these coefficients.

Temperature sensors introduce some transportation lag in the measurements. With sensor energy balance, this lag is taken into the model:

$$\tau \frac{dT_m}{dt} = T - T_m \quad (30)$$

where, T_m is the measured temperature, and $\tau=9$ s is the sensor time constant.

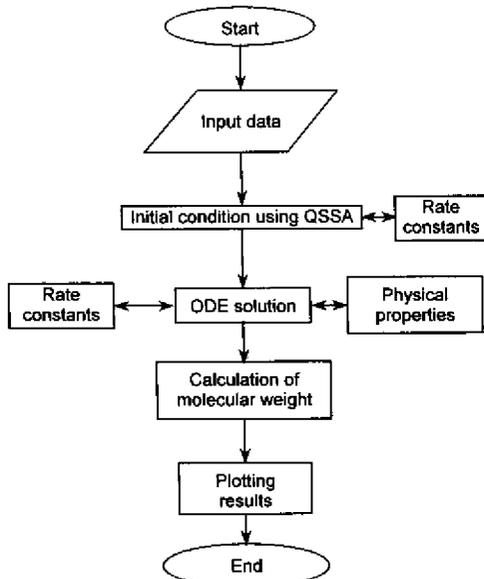


Figure 2. Calculation flow chart.

Solution Method

Eqns (9) – (14) and (28) – (30) are the governing equations of non-isothermal solution polymerization of methyl methacrylate. Overall, fourteen simultaneous ordinary differential equations (ODE) should be solved. This set of ODEs is highly nonlinear and stiff. Therefore, this set is solved numerically. Stiff type equation is the one, which is sensitive to parameter variation. Hence, the time interval should be kept small or the next step error should be estimated not to become unstable. MATLAB 5.3.1 software is used to solve the equations. Figure 2 shows the code flow chart.

RESULTS AND DISCUSSION

Some experiments were carried out to validate the model. These experiments were carried out in three parts. In the first part, some isothermal runs proceeded. Table 5 gives the experimental conditions. Polymerization ran in 90 °C to have shorter time of reaction. The main objective is to obtain a mechanistic relationship between the power, which is fed to the heaters and the reactor temperature.

Therefore, isothermal model is used to find out suitable adjustable parameters θ_p and θ_t . Due to lack of PMMA calibrated GPC, it is preferred to use viscosity average molecular weight. Figure 3 shows the molecular weights comparison. It is known that viscosity average molecular weight is between the number and weight average molecular weights. The calculated polydispersity index is shown too. In the beginning of the polymerization, molecular weights increase because of reaction. After 20 min, molecular weights decrease due to increase in macroradicals and

Table 5. Experimental conditions.

Polymerization condition	
Solvent (mL)	600
Monomer (mL)	150
Initiator	BPO, 0.2 wt % of monomer
Temperature (°C)	90
Mixing speed (rpm)	150

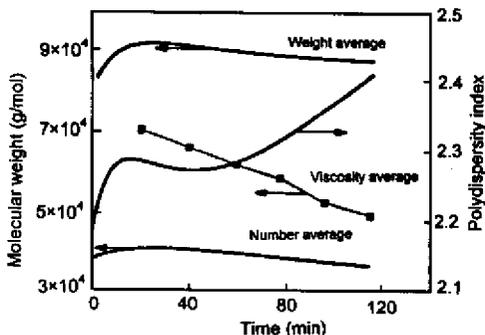


Figure 3. Comparison of calculated and experimental molecular weight during the isothermal polymerization.

consequent increase in the chain transfer reactions. The slope of viscosity average molecular weight is a little more than model predictions for the number and weight average molecular weights. Although, it is believed this is related to under estimation of the chain transfer rate constants, qualitative prediction of model is good. In the next experiments, jacket temperature is taken as the input and process is modelled.

In the second part of the experiments, jacket temperature was changed randomly and the reactor temperature was measured. Figure 4 shows the jacket temperature as the input. Figure 5 shows the calculated and measured reactor temperatures. The simulation result follows the measured value very well. The maximum error is about 5 °C, however, the

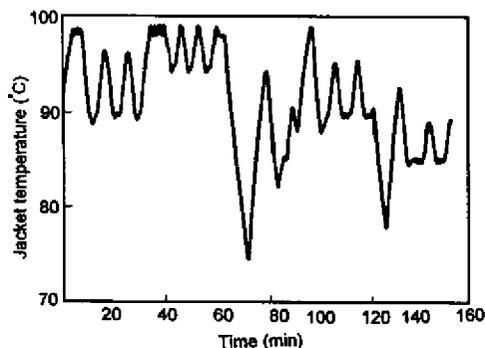


Figure 4. Jacket temperature as input.

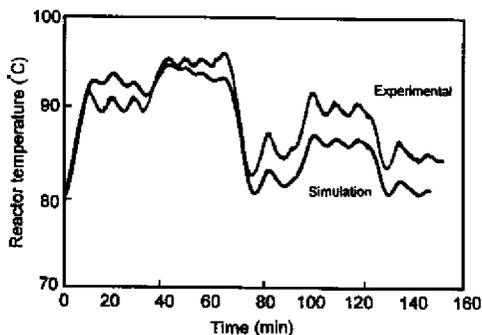


Figure 5. Comparison of calculated and measured reactor temperatures.

mean error is about 2.5 °C. It is believed that the heat transfer coefficients change during the course of the polymerization is responsible for this discrepancy. If a more accurate model is needed, one may use on-line estimation of the heat transfer coefficients according to the method which is presented in the appendix A.

Figure 6 shows the calculated and measured molecular weights. The results have same pattern as the Figure 3. However, increase in molecular weights is obvious. The changes in the molecular weights prove that it is possible to manipulate molecular weight of the final polymer.

As the final part of the experiments, signals to the heaters, and to the valve are sent randomly and the oil bath and reactor temperatures are measured.

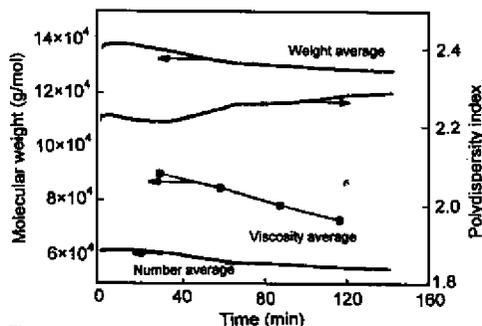


Figure 6. Molecular weights comparison in the non-isothermal polymerization.

Figure 7 shows the signal to the heaters and the on/off valve. In this figure, one in the coordinate axis means full power or open valve and zero means no power or close valve. These signals are given to the model as inputs. Other model variables are calculated. Figure 8 shows the calculated and measured values of jacket

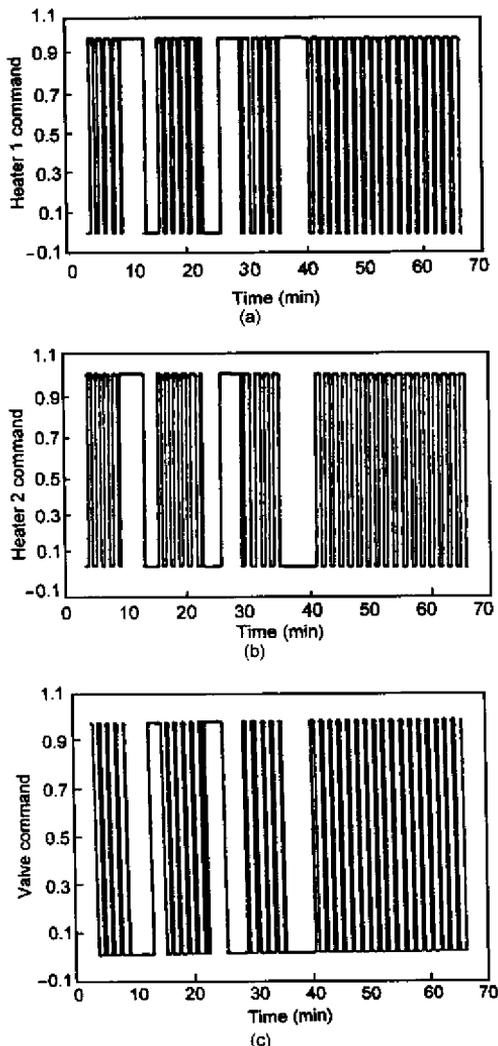


Figure 7. Signals to the heaters and valve.

temperatures. Their agreement is astonishingly good. Therefore, there is no significant change in the heat transfer coefficients of the oil bath during the polymerization reaction.

Figure 9 shows the calculated and measured values of reactor temperatures. Their agreement is good. The maximum error is about 4 °C and the mean error is about 2 °C. Discrepancy between the calculated and measured value of reactor temperatures proves that changes in reactant mixture properties effect the heat transfer coefficients. Furthermore, these results suggest that jacket temperature should be considered as a controlled variable or some kind of constrain in control strategy.

Therefore, the results show a mechanistic

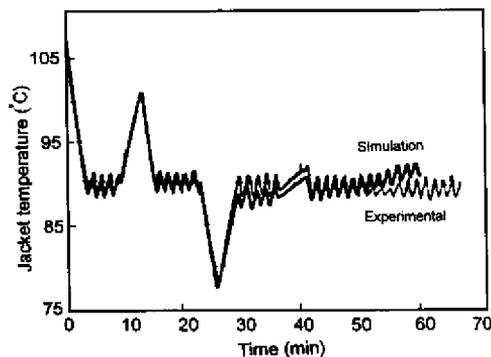


Figure 8. Comparison of jacket temperatures.

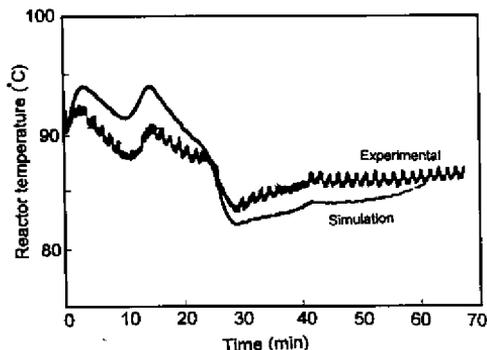


Figure 9. Comparison of reactor temperatures.

relationship between the power, which is fed to the heaters and the jacket and reactor temperatures. One may use this relationship in optimization of the process [12] and control studies.

CONCLUSION

A mathematical model is developed for the batch PMMA polymerization reactor system. In the present model, energy balance is applied to the reactant mixture, oil bath, and temperature sensors. The final model includes fourteen highly nonlinear stiff differential equations. The model predicts monomer conversion, initiator concentration, radical and polymer concentration, volume, and reactor and jacket temperatures. Comparison between calculated and experimental values shows good agreement. Hence, the model is a suitable representation of the process.

The model includes the complete process, therefore, by having the heaters and water valve signals, it is possible to calculate process states. Hence, this model is suitable to find out an optimal temperature trajectory during the course of polymerization and control strategy.

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NOMENCLATURE AND ABBREVIATIONS

C_p	Reactant mixture specific heat
C_{p0}	Specific heat of oil
D	Defined as: $D = \exp[1 - \varphi_p/A + B(1 - \varphi_p)]$
f	Initiator efficiency factor
I	Initiator
k_d	Initialization rate constant
k_t	Transfer to monomer rate constant

k_p	Propagation rate constant
k_s	Transfer to solvent rate constant
k_t	Termination rate constant
m	Reactant mixture mass
m_o	Oil mass
M	Monomer
\bar{M}_n	Number average molecular weight
\bar{M}_w	Weight average molecular weight
PDI	Polydispersity index
P_n^o	Radical consists of n monomer
S	Solvent
t	Time
T	Reactant mixture temperature
T_j	Oil temperature
T_m	Measured temperature
T_w	Coolant water temperature
T_∞	Environmental temperature
$UA _c$	Overall heat transfer coefficient between the oil and the coolant water
$UA _r$	Overall heat transfer coefficient between the reactant mixture and the jacket
$UA _e$	Overall heat transfer coefficient between the reactant mixture and the environment
$UA _{oe}$	Overall heat transfer coefficient between the oil and the environment
V	Instantaneous volume of the reactant mixture.
V_0	Initial volume of the reactant mixture
x	Monomer conversion
α	Heat transfer coefficient between the heater and the oil
β	Is defined as $\beta = \varphi_s / (1 - \varphi_s)$
ε	Volume contraction factor
τ	Sensor time constant
λ_k	Alive polymer chain k^{th} moments
μ_k	Dead polymer chain k^{th} moments
φ_s	Volume fraction of solvent
θ_p	Parameter in the propagation rate constant
θ_t	Parameter in the termination rate constant
$-\Delta H_p$	Heat of polymerization
[]	Concentration of species
0	As subscript means initial condition

Appendix A – Heat Transfer Coefficients Estimation

To estimate $UA|_r$ and $UA|_{oe}$, 750 mL of solvent is put

in the reactor. Mixer agitates the solvent. After a while, heaters turn off and reactor and oil temperatures are recorded. Figure 10 shows these temperatures. Energy balance for the reactor is:

$$mC_p \frac{dT}{dt} = -UA_r(T - T_j) - UA_o(T - T_\infty) \quad (A-1)$$

The linear regression method is used to calculate the heat transfer coefficients. DT/dt is calculated numerically. To eliminate the errors due to measurement, T and T_j are fitted by polynomials. The linear regression result is:

$$\left[\begin{array}{cc} \sum (T - T_j)^2 & \sum (T - T_j)(T - T_\infty) \\ \sum (T - T_j)(T - T_\infty) & \sum (T - T_\infty)^2 \end{array} \right]^{-1} \left[\begin{array}{c} UA_r \\ UA_o \end{array} \right] = \left[\begin{array}{c} mC_p \\ mC_p \end{array} \right] \quad (A-2)$$

$$\left[\begin{array}{c} \sum \frac{dT}{dt}(T - T_j) \\ \sum \frac{dT}{dt}(T - T_\infty) \end{array} \right] \quad (A-2)$$

Finally, heat transfer coefficients are:

$$\begin{cases} UA_r = 47.9238 \\ UA_o = 4.3056 \text{ cal/min}^\circ\text{C} \end{cases} \quad (A-3)$$

To calculate UA_o , while reactor is empty, oil is circulated in the jacket. Heaters turn off and the oil bath temperature is gathered. The energy balance for

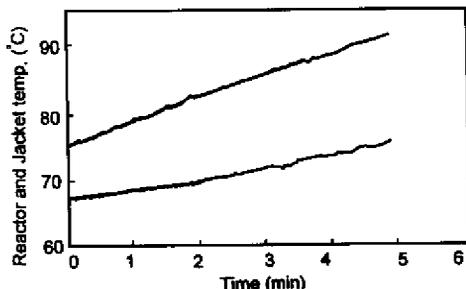


Figure 10. Reactor and jacket temperatures to calculate UA_r and UA_o .

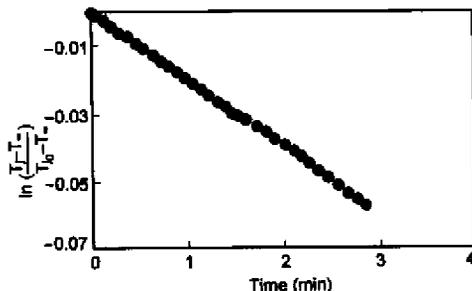


Figure 11. Jacket temperature versus time.

oil in the bath is:

$$m_o C_{po} \frac{dT_j}{dt} = -UA_o(T - T_\infty) \quad (A-4)$$

The solution of this equation is:

$$\ln \frac{T_j - T_\infty}{T_{j0} - T_\infty} = \exp\left(\frac{-UA_o}{m_o C_{po}} t\right) \quad (A-5)$$

Figure 11 shows $\ln(T_j - T_\infty/T_{j0} - T_\infty)$ versus time that is perfectly a straight line. Hence, the initial energy balance eqn (A-4) is correct. The result is:

$$UA_o = 91.0765 \text{ cal/min}^\circ\text{C} \quad (A-6)$$

Similar method gives:

$$UA_c = 162.7305 \text{ cal/min}^\circ\text{C} \text{ and}$$

$$\alpha = 7.6974 \text{ cal/min} \times w \quad (A-7)$$

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