OPTIMIZATION OF SOLUTION POLYMERIZATION OF METHYL METHACRYLATE

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Thesis submitted in partial fulfillment of the requirements
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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Date : JANUARY 2013

Special dedication to my supervisor, my family members,
my friends, my fellow colleague and all faculty members
for all your care, support and believe in me.

ACKNOWLEDGEMENT

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Finally, above all, I feel pleasure to have good health, strength and perseverance to complete this proposal.

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NOMENCLATURE

A	Reactor-jacket heat transfer area, m^2
$A(T)$	Temperature dependent constant in gel effect model
B	Constant in gel effect model
C	Heat capacity of reactant mixture, kJ kg^{-1} K^{-1}
C_i	Concentration of initiator, kgmole m^{-3}
$C_i^*(0)$	Optimal initial concentration of initiator, kgmole m^{-3}
C_m	Concentration of monomer, kgmole m^{-3}
$C_m^*(0)$	Optimal initial concentration of monomer, kgmole m^{-3}
C_s	Concentration of solvent, kgmole m^{-3}
C_w	Heat capacity of water, kJ kg^{-1} K^{-1}
D_n	Dead polymer chain with n unit of monomers
E_i, E_p	Activation energy for initiation and propagation reactions, kJ $kgmole^{-1}$
E_{fm}, E_{fs}	Activation energy for chain transfer to monomer and solvent reactions, kJ $kgmole^{-1}$
E_{po}, E_{to}	Activation energy for the k_{po} and k_{to} respectively, kJ $kgmole^{-1}$
$E_{\Theta t}$, $E_{\Theta p}$	Activation energy for the $k_{\Theta t}$ and $k_{\Theta p}$ respectively, kJ $kgmole^{-1}$
f	Efficiency of initiator
F_{cw}	Inlet flow rate of cooling water, m^3 s^{-1}
F_{cwmax}	Maximum inlet flow rate of cooling water, m^3 s^{-1}
I	Initiator
k_{fm}, k_p	Rate constants for chain transfer to monomer and propagation reactions, m^3 $kgmole^{-1}$ s^{-1}
k_{tc}, k_{td}	Rate constants for termination by combination and disproportionation reactions, m^3 $kgmole^{-1}$ s^{-1}
k_{po}, k_{to}	Overall propagation and termination rate constants at zero monomer conversion, m^3 $kgmole^{-1}$ s^{-1}
k_i	Rate constant for initiation reaction, s^{-1}
$k_{\Theta p}$	Temperature dependent constant in gel effect model

$k_{\Theta t}$	Temperature and initiator loading concentration dependent parameter
in	gel effect model
m	Weight of reactant mixture, kg
M	Monomer
M_i	Molecular weight of initiator, kg kgmole^{-1}
M_m	Molecular weight of monomer, kg kgmole^{-1}
M_n	Number-average molecular weight of dead polymer, kg kgmole^{-1}
M_s	Molecular weight of solvent, kg kgmole^{-1}
M_w	Weight-average molecular weight of dead polymer, kg kgmole^{-1}
P	Input power to heater, kJ s^{-1}
P_{max}	Maximum power of heater, kJ s^{-1}
P_n	Live polymer chain consisting of n monomer units
R	Universal gas constant, kJ kgmole^{-1} K^{-1}
R_m, R_i	Rate of production of M and I, kgmole m^{-3} s^{-1}
S	Solvent
t	Time, s
t_f	Terminal time, s
$T(t)$	Reactor temperature profile, K
T_o	Initial reactor temperature, K
$T^*(t)$	Optimal reactor temperature profile, K
T_{cw}	Temperature of cooling water, K
T_∞	Room temperature, K
T_{gp}	Glass transition temperature of PMMA, K
T_j	Jacket temperature, K
T_{jo}	Initial jacket temperature, K
$\hat{U}$	Single manipulated input obtained by coordinating the two actual manipulated inputs (P and F_{cw})
V	Volume of reactant mixture, m^3
V_o	Initial volume of the reactant mixture, m^3
X_m	Monomer conversion
Z_i	Frequency factor for initiation reaction, s^{-1}
Z_{fm}, Z_{fs}	Frequency factors for chain transfer to monomer and solvent reactions, m^3 kgmole^{-1} s^{-1}
Z_{po}, Z_{to}	Frequency factors for k_{po} and k_{to}, m^3 kgmole^{-1} s^{-1}

$Z_{\Theta t}$, $Z_{\Theta p}$	Frequency factors for parameters $k_{\Theta t}$ and $k_{\Theta p}$, m^3 kgmole^{-1} s^{-1}
$-\Delta H_p$	Heat of propagation reactions, kJ kgmole^{-1}
ε	Volume expansion factor
α	Process parameter
Φ_{mo}	Initial volume fraction of monomer
μ_1	Mass concentration of dead polymer chains, kg m^{-3}
ρ	Overall density of reactant mixture, kg m^{-3}
ρ_i	Density of initiator, kg m^{-3}
ρ_s	Density of solvent, kg m^{-3}
ρ_m	Density of monomer, kg m^{-3}
ρ_w	Density of water, kg m^{-3}

PENGOPTIMUMAN BAGI METHYL METHACRYLATE LARUTAN POLIMERISASI

ABSTRAK

Dalam kajian ini, pengoptimuman untuk dinamik reaktor dan jaket telah dijalankan bagi MMA larutan polimerisasi dengan toluena di kelompok reaktor. Tujuan kajian ini dilaksanakan adalah untuk mengoptimumkan keadaan proses polimerisasi supaya mendapatkan pengubahan yang maksimum dalam masa yang singkat. Kesan gel, kesan kaca, kinetik bukan linear dan tindakbalas yang eksoterma dipertimbangkan dalam proses pengoptimuman. Kecekapan pemula dan pekali pemindaan haba keseluruhan diandaikan kekal malar. Pengoptimuman bagi MMA larutan polimerisasi berdasarkan model tiga peringkat polimerisasi dengan menggunakan perisian MATLAB. Penyelesai Ode23t digunakan dalam menyelesaikan masalah yang serdehana sengit. Keputusan menunjukkan bahawa pengubahan yang tinggi dapat diperolehi pada keadaan dimana kepekatan pemula (AIBN), suhu reaktor dan suhu jaket yang optima. Simulasi bagi MMA larutan polimerisasi dalam kajian ini menunjukkan bahawa MATLAB adalah alat penyelesai yang berkesan dan ekonomi dalam kerja-kerja kejuruteraan.

OPTIMIZATION OF SOLUTION POLYMERIZATION OF METHYL METHACRYLATE

ABSTRACT

In this study, optimization of reactor and jacket dynamics were carried out for the solution polymerization of MMA with toluene in batch reactor. The purpose of this study is to optimize the process condition in polymerization in order to obtain maximum conversion in minimum batch time. The gel effect, glass effect, non-linear kinetic and high exothermic reactions were considered. Initiator efficiency and overall heat transfer coefficient assumed remain constant. Optimization of MMA solution polymerization was based on three stage polymerization model (TSPM) by using MATLAB software. Ode23t solver was used in solving this moderate stiff problem. The results showed that high conversion was obtained at optimum concentration of initiator (AIBN), reactor temperature and jacket temperature. Simulation of the solution polymerization of MMA in this study showed that MATLAB was an effective and economical problem solving tools in engineering works.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Polymer is a common materials widely used in household use, pipeline system, construction, transportation and medical technologies. A polymer is a macromolecule composed of repeating structural units. These sub-units were bonded by covalent force (Cowie and John, 1991). Polymer comprised of natural and synthetic polymers with a wide variety of properties. Natural polymers were such as natural rubber and cellulose which was the main constituent of wood and paper. Synthetic rubber, nylon, polyvinyl chloride (PVC), polystyrene, polymethyl methacrylate and silicone were the synthetic polymers (Lewis et al., 2004).

Methyl methacrylate (MMA) was an organic compound used as monomer to produce versatile polymethyl methacrylate (PMMA). MMA solution polymerization was a free radical chain reaction combine with hydrolysis process. Methanol, benzene, toluene and acetic acid were commonly used as solvent (Semsarzadeh et al., 1997). Polymerization included of three steps which were initiation, propagation and termination. Software was used in this study rather than laboratory testing due to its low costs, no chemical waste, save time, high quality data available and no human error. Optimization of MMA polymerization depends on engineering variables such as temperature, molecular weight of polymer, monomer conversion, initiator concentration and batch time. Manipulated variables were temperature and initiator concentration. The controlled variables were the conversion of monomer.

1.2 Problem Statement

MMA had a big demand in the future and had a very steady growth. This was because PMMA had wide application in many fields such as construction materials, vehicles, signboard and high resistant plastic window such as windows of airplanes. Demand of product depended on quality of product itself. Condition in process can influenced the quality of product. Therefore, selection of best condition for different desired properties of product was the crucial part in optimization. Optimization of MMA solution polymerization was a complex process in chemical and biochemical industry due to its highly non-linear kinetic and exothermic reaction (Hyung-Jun et al., 1998) and (Baillagou and Soong, 1985). Since polymerization was a highly exothermic reaction, it induced a sudden increase in temperature and may cause the thermal runaway effect, low quality product, instabilities and even explosion. Therefore, it was important to control the temperature. Gel effect and glass effect acted as disturbances had been controlled to avoid undesired properties of final polymer product (Lepore et al., 2007). Monomer conversion and polymer molecular weight depended on initiator concentration and reaction temperature. Combination of right type of initiator with optimal composition and the temperature profile was considered in kinetic control to avoid undesired residual and vaporization of monomer if temperature is too high (Gao et al., 2004).

1.3 Research Objectives

i. To develop solution polymerization optimization by using MATLAB.
ii. To optimize temperature and initiator concentration to obtain desired values of conversion in minimum batch time.
iii. Compare results with experimental work by Soroush and Kravaris (1992).

1.4 Scope of the Study

i. To optimize solution polymerization of methyl methacrylate with toluene in the presence of Azo Bis Isobutyronitrile (AIBN) as initiator by using batch reactor.
ii. MATLAB software based on three stage polymerization model (TSPM) was used to obtain optimal initiator concentration and reaction temperature.
iii. Compare with results from the journal by Soroush and Kravaris (1992).

1.5 Expected Outcome

i. Desired monomer conversion can be maximized.
ii. Initiator concentration and reaction temperature can be optimized.
iii. Final batch time for polymerization optimization can be minimized.

1.6 Significance of the Study

Optimization of MMA purposed to obtain the optimal values of condition parameters which can improved the properties of final polymer product. Also, the study was able to reduce the undesired waste generation which fulfill to manufacturer and customer’s demand. Production expenditure was reduced due to the minimization on the batch time during the polymerization.

1.7 Conclusion

Polymer product was widely required especially in engineering field. In order to produce desired degree of polymer product, optimization of polymer properties was the crucial process. Efficient controlling of the optimal condition would give impacts on production time, quality, quantity and economic value to the industry.

CHAPTER 2

LITERATURE REVIEW

2.1 Methyl Methacrylate (MMA)

Methyl methacrylate (MMA), $C_5H_8O_2$ was a colourless, volatile organic compound with a characteristic odor that had been described as fragrant, fruity, acrid and pungent (National Industrial Chemicals Notification and Assessment Scheme, 2009). The purity of commercial MMA is typically 99.9%. It contained traces of acidity as the methacrylic acid and water (Dormer et al., 1998). Figure 2.1 shows the structural of MMA.

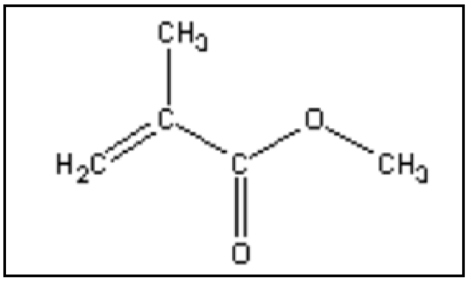


Figure 2.1 Structural of MMA

2.1.1 Chemical and Physical Properties of MMA

The physical and chemical properties of MMA were summarized in Table 2.1 (CHEMFATE, 1994; Ehrenstein, 2001; Evonik Industries AG, Keith and Walters, 1985; 2011; U.S. EPA, 1985; Verschueren, 1983).

Table 2.1 Chemical and Physical Properties of MMA

Properties	**Data**
Physical State	Liquid
Appearance	Colourless
Molecular Weight	100.12 g/gmol
Melting Point	- 48 ℃
Boiling Point	100-101 ℃
Critical Temperature	279 ^{o}C
Critical Pressure	37.5 bar
Critical Volume	0.32 m^3/mol
Water Solubility	15 g/L (25 ℃)
Density	0.939 g/cm^3(20 ℃)
Vapor Density (air=1)	3.45 g/mL
Vapor Pressure	4 kPa (20 ℃)
Viscosity	0.6 cP (20 ℃)
Flash Point	10 ℃
Henry's Law Constant	3.37×10^{-4} atm m^3/mol
Odor Threshold	0.2 mg/m^3
Flammability	Highly flammable

2.1.2 Synthesis of MMA

MMA was commercially manufactured by a number of routes. Figure 2.2 shows the routes to MMA. In acetone cyanohydrin (ACH) route, acetone and hydrogen cyanide were used as raw materials. MMA was produced from isobutylene (TBA) which was sequentially undergo two stage gas phase oxidation from TBA to methacrylic acid, followed by esterification (Bauer, 2000). MMA could be prepared from methyl propionate and formaldehyde too (Nexant Chem System, 2006). For the new development, the Lucite-Alpha process relied on combined carbonylation and esterification of ethylene to methyl propionate. Methyl propionate reacted with formaldehyde under almost anhydrous conditions to form MMA (Nexant Chem System, 2006).

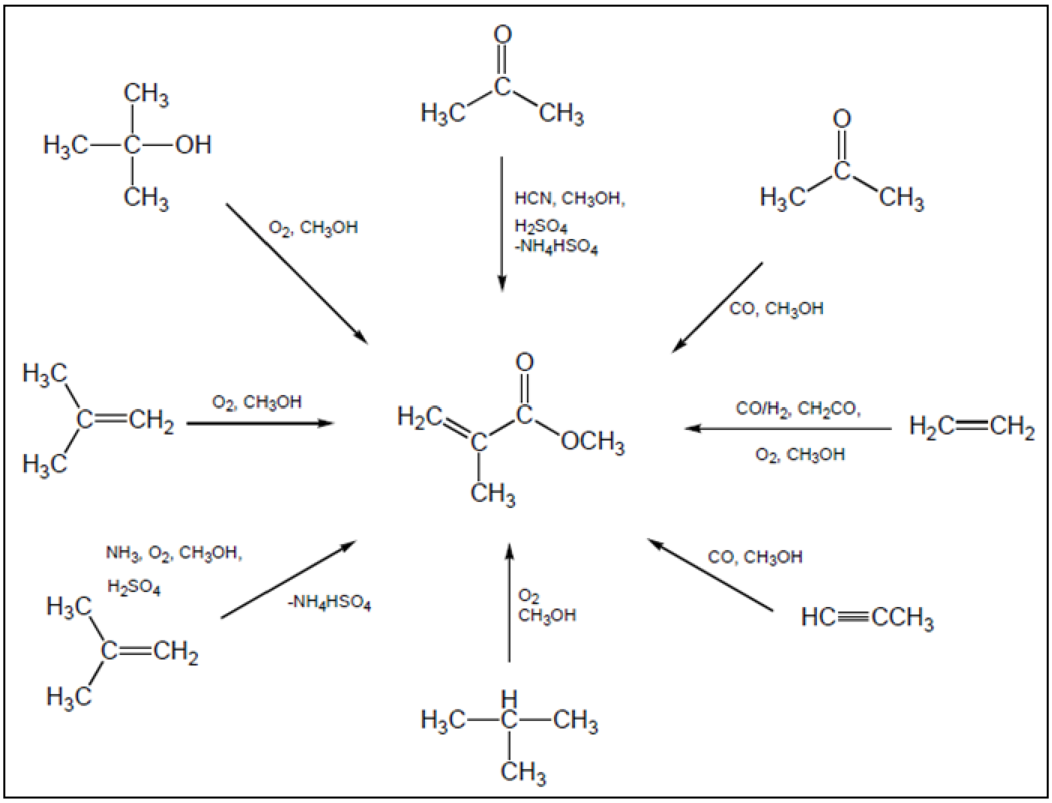


Figure 2.2 Routes to MMA

2.1.3 Global Production of MMA

At the present growth rate, capacity utilization of MMA was estimated exceed 90 percent in United State (Johannes, 2005). World consumption of MMA was over 2 million tons in 2002, valued at approximated US $1 billion. World markets were currently oversupplied because of the heavy buildup in overseas capacity, especially mainly in China and Southeast Asia. The global market for MMA was forecast to reach a consumption volume of 3.2 million metric tons by the year 2017 (Jose, 2012). Electronics was the fastest growing end-use sector of MMA and PMMA globally, particularly in Asian markets of China, Taiwan and Korea. Persistently rising LCD market had been creating strong demand for the worldwide MMA market. Figure 2.3 shows the global demand and supply of MMA from year 2003 until year 2007 (Koichi and Toshiaki, 2004).

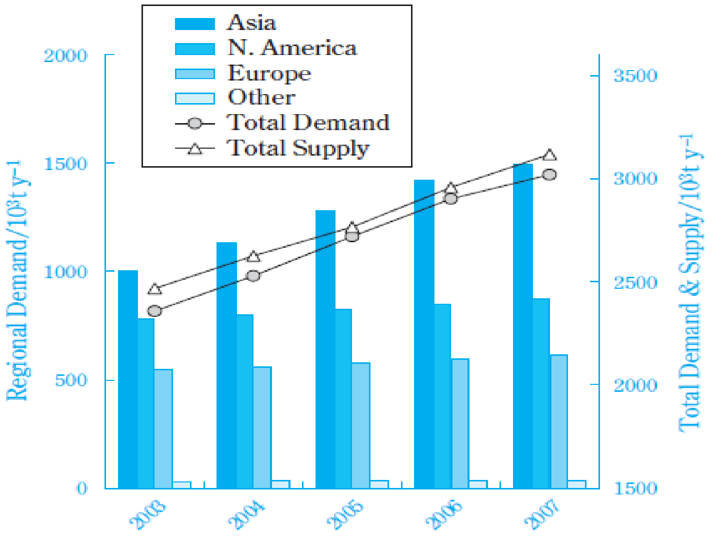


Figure 2.3 Global Demand and Supply of MMA from year 2003 to 2007

2.1.4 Application of MMA and PMMA

MMA was a volatile synthetic chemical that was produced for the use as monomer in the large scale production of polymers and as intermediate for synthesis of other methacrylate esters. MMA principally was used in the production of acrylic plastics and resins for sheeting and molding compounds, which were used in construction, transportation, consumer products and industrial applications and in making signs (Dormer et al., 1998).

Polymethyl methacrylate (PMMA) was a versatile material and had been used in a wide range of fields due to its clarity, lightweight and resistance to the effect of UV light and weathering. PMMA was used in the lenses of exterior lights of transportation (Kutz and Myer, 2002). PMMA was an important improvement in the design of aircraft windows, making possible such iconic design as the bombardier's transparent nose compartment in the Boeing B-17 Flying Fortress. In orthopedic surgery, PMMA bone cement was used to affix the implants and to remodel the lost bone. It was supplied as a powder and with MMA liquid to yield dough-like cement that gradually hardens (Miller, 1996). Other than that, PMMA in a purified form was used as a matrix for solid state dye lasers (Duarte, 2009).

2.2 Toluene

Toluene (C_7H_8) was a volatile and reactive organic with typical odor as sweet, pungent and benzene-like (NIOSH, 1994). It was an aromatic hydrocarbon that was nearly insoluble in water. However, it was miscible with alcohol, acetone, benzene, ether and others organic solvents (HSDB, 1996). Toluene was widely used in gasoline blending, but also as a solvent for paints, adhesives and industrial feedstock (Parker, 1999). Figure 2.4 shows the structural of toluene.

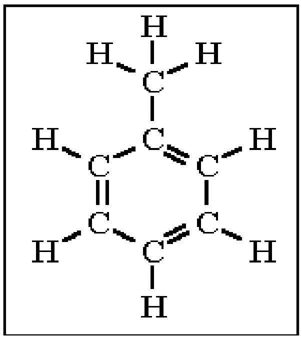


Figure 2.4 Structural of Toluene

2.2.1 Chemical and Physical Properties of Toluene

Table 2.2 below shows the chemical and physical properties of toluene (Budavari et al., 1989; Evonik Industries AG, 2011; Hawley, 1981; Keith and Walters, 1985; NIOSH, 1994; U.S.EPA, 1985; U.S. Air Force, 1989; Verschueren, 1983).

Table 2.2 Chemical and Physical Properties of Toluene

Properties	**Data**
Physical State	Liquid
Appearance	Colourless
Molecular Weight	92.13 g/g mol
Melting Point	-95 ℃
Boiling Point	110.6 ℃
Water Solubility	515 mg/L (20 ℃)
Density	0.87 g/mL (20 ℃)
Vapor Density (air=1)	3.14 g/mL
Vapor Pressure	22 mmHg (20 ℃)
Specific Heat	1.717 KJ/kg K (20 ^{o}C)
Thermal Conductivity	0.141 W/m K
Viscosity	0.59 cP (20 ℃)
Flash Point	4.4 ℃
Henry's Law Constant	6.61x10 atm m^{3}mol
Odor Threshold	2.9 ppm (in air)
Flammability	Inflammable

2.2.2 Synthesis of Toluene

Toluene occurs naturally at low levels in crude oil and was usually produced in the process of ethylene cracking or making coke from coal. In final separation, distillation or solvent extraction takes place for toluene extraction. While from Friedel-Crafts reaction, benzene reacts with methyl chloride in the presence of anhydrous aluminium chloride to form toluene (HSDB, 1996). Other method was toluene sulfonic acid treated with superheated steam or boiled with hydrochloride to form toluene.

2.2.3 Global Production of Toluene

Almost all toluene was derived from petroleum processing and most of that was unrecovered. This toluene estimated exceed 455000 tonnes annually were incorporated directly into gasoline (U.S. EPA, 1990). There were 20 toluene-producing companies in the US which were BP Chemicals, Koch Industries, Lyondell Petrochemical, Marathon Oil, Triangle Refining and others companies. Annual production capacity for toluene was estimated 4932000 tonnes (Mannsville 1992). Demand for toluene in the world was expected to experience modest growth over the next several years.

2.2.4 Application of Toluene

Same as others organic solvents, toluene was widely used as solvent in chemical field. It was used in aerosol spray paints, inks, adhesives, natural gums and resins (HSDB, 1996). Toluene could be used as an octane booster in gasoline, as a raw material for toluene diisocyanate, and in extraction processes (U.S. EPA, 1995). Toluene was another group of fuels that had recently been used as components for jet fuel surrogate blends due to its content of aromatic compounds (Ji and Egolfopoulos, 2011). Other than that, toluene had also been used in the process of removing the cocaine from coca leaves in the production of coca-cola beverage (Merory and Joseph, 1968).

2.3 Azo Bis Butyronitrile (AIBN)

Azo bis isobutyronitrile (AIBN) was a white, odorless crystalline solid with molecular formula $C_8H_{12}N_4$. It was almost insoluble in water and had poor solubility in methanol, ethanol and diethyl ether. But, it had a good solubility in acrylonitrile, chloroform and methyl methacrylate (Verschueren, 1983). AIBN was safer than other catalyst such as benzoyl peroxide due to its lower risk of explosion and no oxidation by-products is formed (Smiley, 1981). Figure 2.5 shows the structural of AIBN.

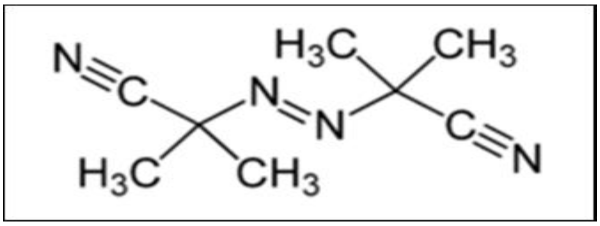


Figure 2.5 Structural of AIBN

2.3.1 Chemical and Physical Properties of AIBN

Table 2.3 shows the chemical and physical properties of AIBN (Barsky, 1976; Merck Index, 1981; NLM, 2000; Smiley, 1981; Verschueren, 1983).

Table 2.3 Chemical and Physical Properties of AIBN

Properties	**Data**
Physical State	Solid (STP)
Appearance	White crystalline
Molecular Weight	164.21 g/g mol
Humidity	Maximum 2%
Boiling Point	236.2 ^{o}C (760mmHg)
Melting Point	103 ℃
Flash Point	96.6 ^{o}C
Water Solubility	350 mg/L (25 ℃)
Density	1.1 g/mL (20 ℃)
Vapor Pressure	0.05 mmHg (25 ℃)
pH	7.0 ± 0.5
Flammability	Flammable

2.3.2 Synthesis of AIBN

AIBN was industrially prepared by treatment of acetone cyanohydrins with ammonia or hydrazine followed by oxidation of intermediate product with sodium hypochlorite, NaOCl or molecular chlorine, Cl_2 (NLM, 2000). Figure 2.6 shows the preparation of AIBN from Acetone Cyanohydrins.

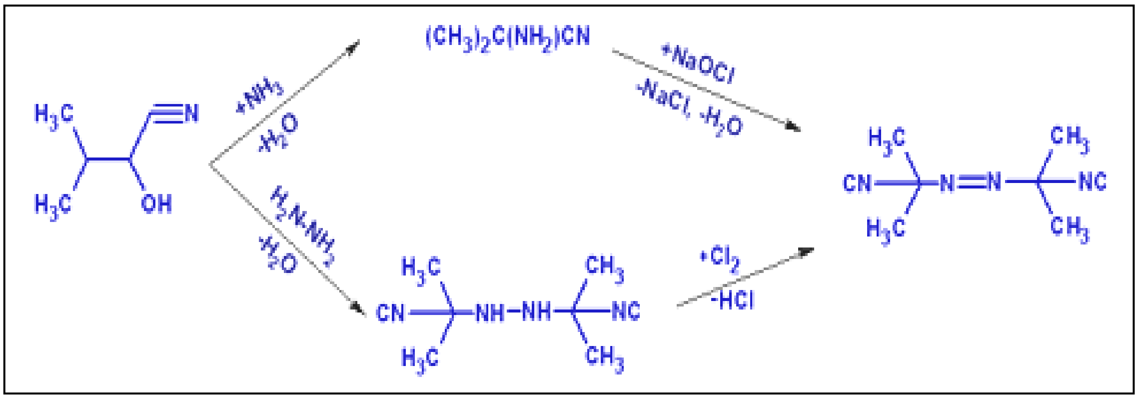


Figure 2.6 Preparation of AIBN from Acetone Cyanohydrins

2.3.3 Global Production of AIBN

The production capacity of Azo catalyst in Japan is 1,100 tonnes per year in 1995 and 12 tonnes were imported. All of Azo catalyst produced and imported in Japan was used as a foaming agent for rubber and an initiator of polymerization, and no consumer uses were reported by Smiley (1981).

2.3.4 Application of AIBN

Azo initiators were mainly used in polymerization reactions to initiate or terminate the polymerization process or to reduce the residual monomer content. It polymerized MMA, styrene, and vinyl chloride (Smiley, 1981). Their possible applications cover many fields. The common applications were in copolymerization of vinyl compounds, acrylic sheets and coating resins. It also can be used as catalyst for free radical halogenations or sulphochloration and as a blowing agent for plastics and elastomers (Smiley, 1981). Figure 2.7 shows the conversion of MMA to PMMA by AIBN.

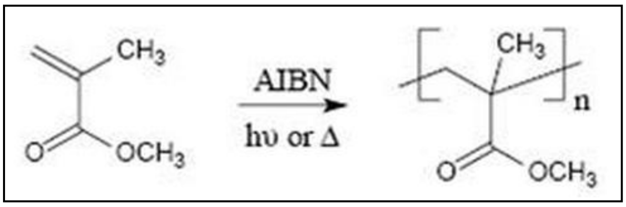


Figure 2.7 Conversion of MMA to PMMA by AIBN

2.4 Chemistry of Solution Polymerization

Polymerization was a process to which small molecules combine to each other to form long chain polymer molecules (PMMA). These small molecules were called monomers (MMA). There were different classes of polymerization. In this study, chemical-initiated free-radical polymerization of methyl methacrylate (MMA) was considered to occur in a batch process. Solution polymerization of MMA was in the category of free-radical polymerization due to its active center was a free-radical (Kiparissides, 1996). This system followed the standard kinetic scheme, which included the formation of reactive radicals by decomposition of the initiator (AIBN), the reactive addition of monomer units to radical polymer chains in the propagation stage, deactivation of polymer radicals by reaction with other polymer radicals in the termination stage and chain transfer to monomer.

Solution polymerization involved monomer, initiator and solvent. Monomer and solvent were added to the process at beginning. The detail process for polymerization three basic steps (initiation, propagation and termination) was discussed in next section. In this study, toluene was added as solvent to reduce potential viscosity or the mixing problem. Solution polymerization was versatile and amenable to temperature control (Hocking, 2005). Figure 2.8 shows the chemistry of solution polymerization (Source: NITTO DENKO CORPORATION).

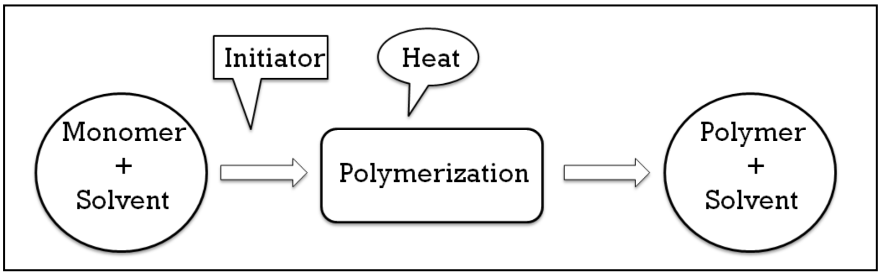


Figure 2.8 Chemistry of Solution Polymerization

2.4.1 Initiation

Initiation was the first step in polymerization where Azo Bis Isobutyronitrile (AIBN) initiates the chain growth. Figure 2.9 shows the reaction of AIBN decomposition under heating (Clarkson, 2012). Once initiator (AIBN) decomposed into free radical form, the radical in AIBN site will tried to collect electron from the nearest convenient source. MMA molecules consisted of weak double bond, so radical in AIBN site was easily to attacked it and form a free radical chain. This situation was illustrated in Figure 2.10 (Clarkson, 2012).

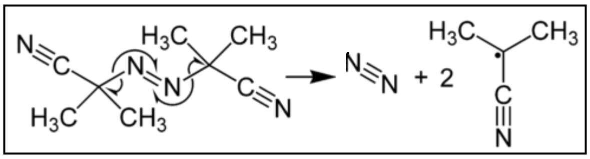


Figure 2.9 Decomposition of AIBN

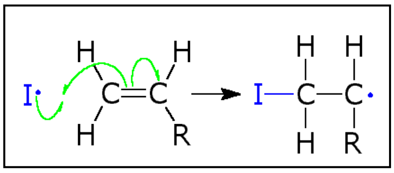


Figure 2.10 Reaction of Initiator Radical with Monomer unit

2.4.2 Propagation

Propagation step was a process where the free radical chain formed by initiation reaction reacts to MMA molecules to form a new free radical chain. Subsequence grow where ends of two propagating chains linked together to form a long chain molecules with thousands of links. These long chain molecules were PMMA. Figure 2.11 was the reaction mechanism on how the initial step of propagation reaction occurs (Clarkson, 2012).

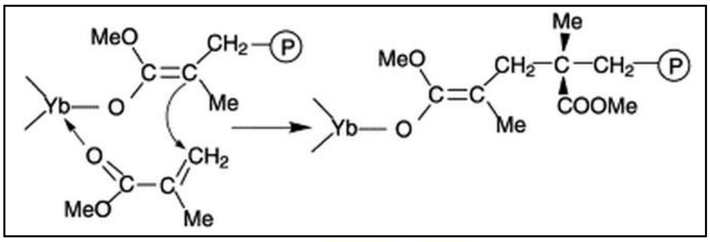


Figure 2.11 Reaction Mechanism for Initiation of MMA Polymerization

2.4.3 Termination

In polymerization, there were thousands of MMA joined together to form longer chain polymers (PMMA). Since there were a lot of free radicals around, they were likely to move into each other and combined to generate a new bond. Once the new bond formed between PMMA, the long chain was terminated. This situation where the chain growth was stopped was called combination termination and was shown in Figure 2.12 (Key Centre for Polymer Colloids, 2001). Figure 2.13 shows the others type of termination method was disproportional termination which is complex (Clarkson, 2012). During disproportional termination, one terminated chain will have an unsaturated carbon group while another terminated end was fully saturated.

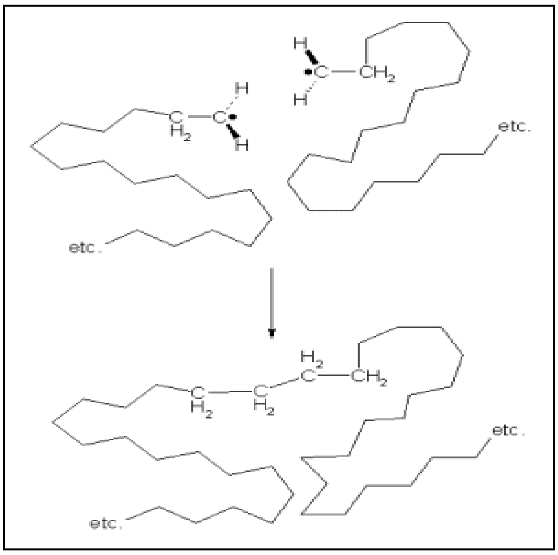


Figure 2.12 Combination Termination of Polymer

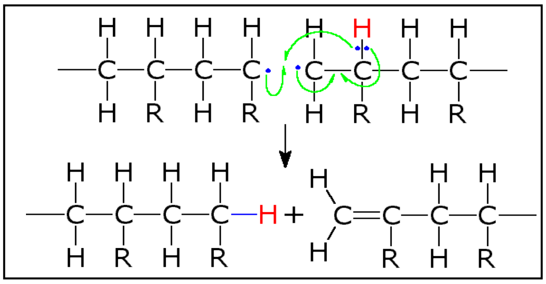


Figure 2.13 Disproportionation Termination of Polymer

According to the theory established by Chiu et al. (1983), the termination takes place in three steps:

i. Polymer radicals initially separated by more than one molecular diameter approach by translational diffusion.

ii. Ends of radical chain moved toward each other (segmental diffusion).

iii. Termination reactions take place after the proper orientation of the chains to each other.

2.5 Three Stage Polymerization Model (TSPM)

TSPM was included low conversion, gel effect and glass effect stages. Gel and glass effects were exhibited in the solution polymerization of MMA. Low conversion stage was a process where the monomer conversion was lower than the desired monomer conversion. Gel effect and glass effect were disturbances and may produce uncertain amplitude (Lepore et al., 2007). If both of these effects were ignored, the final polymer product with poor properties and the low monomer conversion will produced.

2.5.1 Gel Effect

When the monomer conversion was sufficient, gel effect would occurs (Lepore et al., 2007). Gel effect was a phenomenon that strongly depended on process condition and solvent content but does not significance influenced by type of reactor used in polymerization process, either batch, semi-batch or continuous reactor.

In the modeling of MMA solution polymerization, gel effect was one of the most important factors should be concerned. It was a sudden increase in rate of free radical polymerization and viscosity of the reacting medium. Also, gel effect arises when there was a sufficient high monomer conversion. At high conversion, amount of polymer in the system would increases and thus space between molecules would become limited. This leads to difficult movement where diffusion resistance to radical growth was rise. Because of gel effect was exhibited during the diffusion controlled termination, this effect can cause depolymerization and equipment plugging (Biondi et al., 2010).

2.5.2 Glass Effect

Glass effect stage was exhibited only when there was a very high conversion of monomer and the reaction temperature was lower than its glass transition temperature (T_g). T_g was the temperature where the polymer changes from an amorphous glass state to a viscous melt which comes along with the changes in its physical properties (Philip, 2006). T_g of commercial grades of MMA was various due to its chemical compositions. Research in Wei'an et al. (2003) shows that T_g of pure MMA was within range of 90 to 120 ^oC. Dixit et al. (2009) reported that T_g of pure MMA is between 80 to 110 ^oC. The range is so wide because of the vast number of commercial compositions which were copolymers with co-monomers other than MMA. Similar with gel effect, diffusion resistance to the movement of monomer toward a growing radical was increase. Thus, propagation reaction started to decrease and the polymerization tends to be stop before all of the monomer was fully consumed.

2.6 Effect of Solvent

Solution polymerization was one type of polymerization processes. There was a different between solution polymerization with other type of polymerization where the solvent was added to the process. In this study, toluene was used as solvent in the polymerization process. Toluene was aid in efficient heat transfer. When the reactants are mixing together, a cluster was formed. This cluster rises up the viscosity of reacting medium and influence the rate of polymerization. At the same time, mixing of reactants released amount of heat and lead a high exothermic condition. In order to avoid the process being affected, toluene added to the process. Toluene absorbs the heat released and evaporates to remove the heat. Therefore, temperature can be easy to be controlled.

Presence of solvent in polymerization had an important positive impact on the reaction stability in terms of avoiding the strong gel effect since it was a viscosity related phenomenon (Philip, 2006). By adding fixed quantity of solvent, polymer content reduced. This leads into reduction in viscosity of solution and thus gel effect decreased too. Other than gel effect, addition of solvent affected the molecular weight. As the quantity of solvent added was increase, the final molecular weight of polymer decreased due to the reduction of polymer content.

Viscosity was one of the crucial parts in polymerization process, it give effects on the polymerization kinetics, heat transfer and even pressure drop in reactor. Viscosity also affected by polymer weight. Higher molecular weight give higher viscosity due to the high quantity of atoms packed together. To solve this problem, addition of solvent to the polymerization reaction was the best solution which reduced the viscosity of reacting medium by reduction of polymer content in the mixture.

2.7 Effect of Initiator

2.7.1 General Function of AIBN

AIBN was the best known azo initiators which were easy and safe to be used in the catalytic free-radical polymerization in the operation temperature range of 45 to 90 ^{o}C, a primary criterion in controlling the polymerization reactions. AIBN decomposed into two radicals by absorbed thermal energy provided from the system.

The rate of free-radical formation can be controlled by adjusting the operation temperature. AIBN does not cause oxidative degradation and discoloration which maintain physical properties of polymers (Ehrenstein, 2001).

2.7.2 AIBN Concentration

Decomposition of AIBN molecules at the beginning process was primary depended on the AIBN efficiency. High efficiency of AIBN improved its ability to decompose. Since part of AIBN had a reaction with other reactants in the system and self termination, thus, initiator efficiency will less than 100%. This means that small portion of AIBN was remained in reactor. Concentration of initiator (AIBN) had a very strong impact on the conversion evolution in the batch polymerization reactor. Philip (2006) stated that, when initiator concentration increased, reactor behavior becomes unstable and the reaction was more prefer goes to the gel effect. However, increased the initiator concentration did not change much on the average molecular weight. Since AIBN had low molecular weight and freedom from side reactions, it was more efficiency and economical for controlled polymerization at the low concentration. Figure 2.14 shows the conversion of AIBN various with the concentration of monomer.

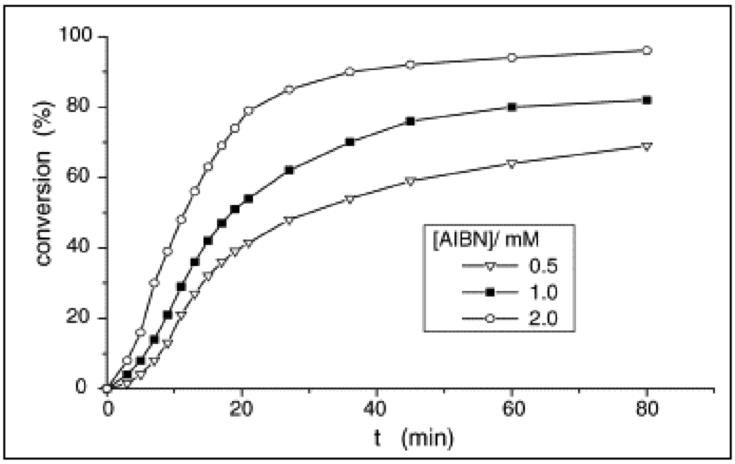


Figure 2.14 Effect of AIBN Concentration on Monomer Conversion

2.8 Effect of Process Temperature

Process temperature had important impacts on both polymerization kinetics and polymer properties. In this study, batch reactor temperature and jacket temperature were detailed discussed in following section.

2.8.1 Reactor Temperature

Temperature was a very important parameter in solution polymerization of MMA. Process condition and final properties of polymer product were significance influenced by reactor temperature. Temperature of reactor gave impacts on conversion, gel effect, termination, viscosity and molecular weight of polymer.

Reactor temperature had strong effect on the gel effect. The gel effect intensified as the reaction rate increased due to increased in temperature. Or in another words, polymerization rate increased (monomer conversion increase too) at high temperature, so gel effect increased since it was exhibited by sufficient high conversion. This was because of the rapid increased of initiator decomposition rate as well as an increased of the propagation rate with temperature. The relationship between process temperature and conversion was illustrated in Figure 2.15 (Philip, 2006). At high temperature, amplitude of the gel effect diminished, and de-polymerization may be appeared.

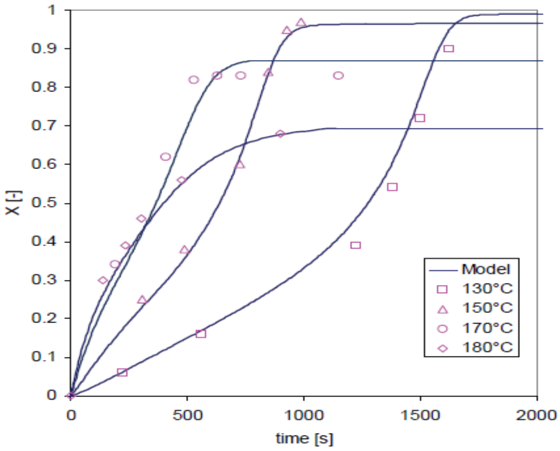


Figure 2.15 Modeled and Experimental Conversion for Different Temperatures

After certain polymerization reaction, polymers started to be decomposed by scission of head to head bonds at highly temperature. Unstable bonding force in polymer was broken by increasing the process temperature. Moreover, by increasing temperature, termination reaction by combination and disproportionation were preference to be occurred (Philip, 2006).

According to the research in (Philip, 2006), viscosity of reacting medium was affected by process temperature. At sufficient high temperature, concentration of reactant became lower; molecular weight of polymer decreased. Since the polymer content decreased, viscosity of reacting medium was low and allowed the polymer flow smoothly without any large barrier. Thus, high temperature gave lower molecular weight and lower viscosity. This showed that temperature was required to be control well since it gave significance impacts on various parameters.

2.8.2 Jacket Temperature

Since the environment of polymerization reactions was mostly in the viscous condition, certain of high molecular weight polymer deposited on the reactor wall and lead to the raise in viscosity. This highly viscosity medium can limited the heat transfer and make the temperature drops at the outlet zone of reactor. At this condition, heat was released from the system to atmosphere. The condition where the heat needed to be removed from the system was called exothermic reaction.

Polymerization was a very fast and exothermic reaction ($-\Delta H_p = 57.8\ KJ/mol$), which comes along with strong raise in viscosity. The reaction kinetics was strongly influenced by gel effect. Heat removal capacity must be sufficient to avoided thermal runaway of the reaction in the reactor. To make sure the temperature of reactor was under controlling, a jacket system was required. In this study, jacket was functions to controlled and maintained the reactor temperature closed to the set point.

2.9 Optimization

2.9.1 Principle of Optimization

Practically, optimization was defined as “To find the best solution for any process or problem within its constraints. The significance step in the development of an optimum design was to determine the objectives of the optimization and what factors or variables were to be optimized. The common objective of optimization was to define the best solution or condition for the problems.

In optimization, there were various terms were used to simplify the discussions and explanation. Firstly, design variables were those independent variables over which the engineer had some control (Richard et al., 1998). Secondly, objective function was a mathematical function for the best values of the decision variables to reaches a minimum or a maximum (Richard et al., 1998). When the measurement can bring to profit, engineers had to formulate the strategy to maximize it but when it was a costly process, they should come out with solution to minimize it. Thirdly, constraints were the limitations or boundary on the values of decision variables which can be divided into equality constraint and inequality constraint (Richard et al., 1998). This means that each variable has their optimum range in a specific condition. Thus, it was important to determine its constraint in order to prevent the condition affect the overall process as well as the final product. Therefore, optimization can be simply defined as a solving tool to identify the maximum and minimum value of a solution.

Optimization was the engineer's work to improve the initial design of process condition and strive to enhance the operation of that process (Thomas and David, 2001). Optimization can bring a lot of benefits for a plant. For examples, optimizing plants operation conditions and performance can enhance productivity, bring greatest profit, reduce expenditure cost and save time.

2.9.2 Optimization in Batch Polymerization Reactor

Process optimization had a significant impact on polymer plant operability and economics. Polymer production facilities faced increasing pressures to reduce operation cost and achieve high quality. The main property of polymer products was correlated with molecular weight distribution. This was an important parameter to characterizing polymer quality which can be controlled by adopting a suitable operating condition for the reactor and by choosing the initial conditions of the operation.

In this study, solution polymerization of MMA was using batch reactor. The batch polymerization technique was widely used in industry for its availability and flexibility in operation. Batch reactor was a less auxiliary, cheaper and less elaborate control system (Ray, 1986). Jacket of the batch reactor was required to control the highly exothermic polymerization process. Jacket set point was set to prevent undesirable temperature overshooting and oscillations (Crowley and Choi, 1996). The objective of this study was to optimize the reaction temperature and initiator concentration in order obtained a maximum monomer conversion and maintained polymer molecular weight at desired values.

If reaction temperature was too low or lower than its glass transition temperature (T_g), glass effect was occurred. In high temperature, productivity of polymer can be enhanced and decreasing of the batch time. However, if heating temperature was too high, temperature overshoot and thermal runaway may occurred (Crowley and Choi, 1996). This may leads to low performance of optimal controller and increased the operation cost.

In this study, AIBN was an initiator in MMA solution polymerization. Concentration of initiator can affects the final polymer product properties. AIBN will just affects on initiation reaction but not in propagation and termination reactions. In the research of Cheng et al. (2006), when initiator concentration increased, polymerization rate constant increased, induction periods will decreased and the polymerization rate will increased. Henini et al. (2012) showed that the reaction and the monomer conversion increases when initiator concentration increase. Molecular weight of polymer will decrease in high initiator concentration because the reaction between monomer with the initiator (Ibrahim et al., 2011).

There have been many attempts to optimize the batch polymerization because of the numerous and complex problems involved. Different types of optimization problems regarding objectives and decision variables, mathematical solving methods, and mathematical models included in the optimization procedure, as well as the recent problem of multi-objective optimization accomplished in a vector or scalar fashion. In order to effectively control the polymer quality, global optimization required the achievement of high productivity (high conversion, short reaction time) and respect for operations safety.

2.10 MATLAB Software

MATLAB had a complete name that was MATrix LABoratory. It was an advance computer system that provides a convenient environment for handling scientific and engineering problems (Hahn, 2002). MATLAB had been widely application in the field of scientific, mathematical and engineering to solve the daily problems such as operation condition in plant and design work. Besides that, this software also popular applied in research project especially for simulation, optimization and experimental work. MATLAB had great efficiency and effectiveness in developing calculations in shorter time. It had a number of optional toolboxes that provide specialized functions including signal processing, control system, system identification, optimization and statistics (Chapra and Canale, 2006).

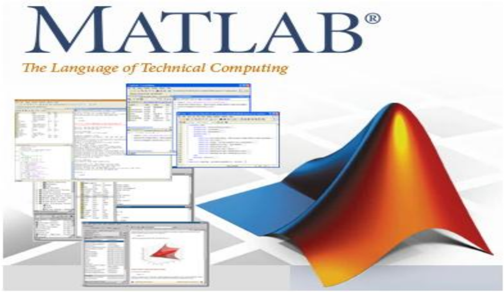


Figure 2.16 MATLAB Software

2.10.1 Numerical Computation

Numerical method was a technique by which the mathematical problems were formulated so that they can be solved with arithmetic systems. There were many types of numerical methods, but all of them had one common characteristic that was invariably involved large numbers of tedious arithmetic calculations (Chapra and Canale, 2006). Numerical method was a powerful problem-solving tool. It was able to handle large system of equations, nonlinear problems and complicated geometries that were often impossible to solve analytically. Recently, the role of numerical methods in engineering problem solving had been increased dramatically with the development and efficiency in digital computer.

2.10.2 Ordinary Differential Equation (ODE)

Ordinary differential equation (ode) was very important in the engineering practice because many physical laws were couched in terms of the rate of a quantity rather than the magnitude of the quantity itself (Chapra and Canale, 2006). The common term for ode was $\frac{dy}{dt}$ where “y” was the quantity or parameter that we needed to be measured while “t” was the time required for the process to run. Sometime, this term was called as the changed of such parameter in given time or rate of change. Generally, two types of problems were addressed in ode that was initial value and boundary value problems.

2.10.3 ODE Solver

MATLAB ODE solver was used to implement the numerical integration methods. Started at the initial time with initial conditions, it stepped through the time interval and computed a solution at each time step (Chapra and Canale, 2006). Once the solution for a time step satisfied to the solver's error tolerance criteria, it was a successful step and can be continue to next step. But, if there was any small mistake on keying the input data, it was a failed attempt, the solver will shrinks the step size and the procedure have to tries again (Chapra and Canale, 2006). Therefore, any even a very small error was necessary to be avoided since it was very sensitive.

ODE solver was divided into two categories that were non-stiff solver and stiff solver. Stiffness as a special problem that can be arises in the solution of ode. There were three types of solvers designed for non-stiff problems such as ode45, ode23 and ode113. Non-stiff solver just can solve the simple problems. Normally, ode45 was recommended to be used as first solver for a problem. If those three non-stiff solvers failed to solve the problems, stiff solver was required. Stiff solvers were designed to solve the difficult problems which cannot be solved by the non-stiff solvers. A stiff system was the one involving rapidly changing components together with slowly changing ones. There were four solvers designed to solve the stiff problems such as ode15s, ode23s, ode23t and ode23tb. A summary of choosing a suitable solver was shown in Table 2.4 (Shampine and Reichelt, 1997; Shampine, 1994).

Table 2.4 Summary of Various ODE Solvers

Solver	**Type**	**Accuracy**	**Use**
ode45	Nonstiff	Medium	Majority used. First solver should be tried.
ode23	Nonstiff	Low	For crude error tolerances or moderately stiff problems.
ode113	Nonstiff	High	Stringent error tolerances or computationally intensive ODE file.
ode15s	Stiff	High	For stiff system which ode45 cannot solve it.
ode23s	Stiff	Low	Crude error tolerances to solve stiff systems or there was a constant mass matrix.
Ode23t	Moderately stiff	Low	For moderately stiff problems if a solution without numerical damping was required
ode23tb	Stiff	Low	Crude error tolerances to solve stiff systems

2.10.4 Ode 23t

At the beginning, the problem was solved started with ode45 to determine its stiffness. When using ode45 solver, the MATLAB program was too slow and no result was come out. Thus, ode23t was tried to solve the problem. In the very short duration, the results were obtained. As statement in previous section, ode23t was one of the common moderate stiff ode solvers. Ode23t was designed to handle the low to moderate order problems.

2.10.5 Input Arguments

Ode23t usually invoked from the command line in the form of [t,y] = ode23t (‘odefun’, tspan, *y0*). Table 2.5 below showed the meaning of each argument used during MATLAB programming (Shampine and Gordon, 1975).

Table 2.5 Descriptions on Input Arguments

Input Argument	Description
Ode function	Name of the ODE file. A MATLAB function used to evaluates the right hand side of the differential equations at a given value of the independent and dependent variables. All types of solvers can solve the systems of equations in the form where $\frac{dy}{dt}$ = $f(t,y)$.
t	Independent variable such as time, position and volume.
y	A vector of dependent variable such as temperature, position and concentration.
tspan	A vector specifying the interval of integration, [t_0, t_f]. For a two-element vector tspan=[t_0, t_f] , the solver imposes the initial conditions at t_0, and integrates from “t_0” to “t_f”. For tspan vector with more than two elements, the solver returns solutions at the given time points.
t_0	Initial time for the systems in unit of second.
t_f	Final time for the systems in unit of second.
$y0$	A vector of initial conditions for the problem.

CHAPTER 3

METHODOLOGY

3.1 Introduction

Objective of this research was to optimizing the reaction temperature and initiator concentration in order to obtain desired monomer conversion. After developed the polymerization models, MATLAB ode23t solver was used to solve the nonlinear kinetics. This chapter focused on achievement of the optimizing, analyzing and completion of the project. The models were adopted by Soroush and Kravaris (1992). The procedure to be implemented in this study to solve the problems was presented in Figure 3.1.

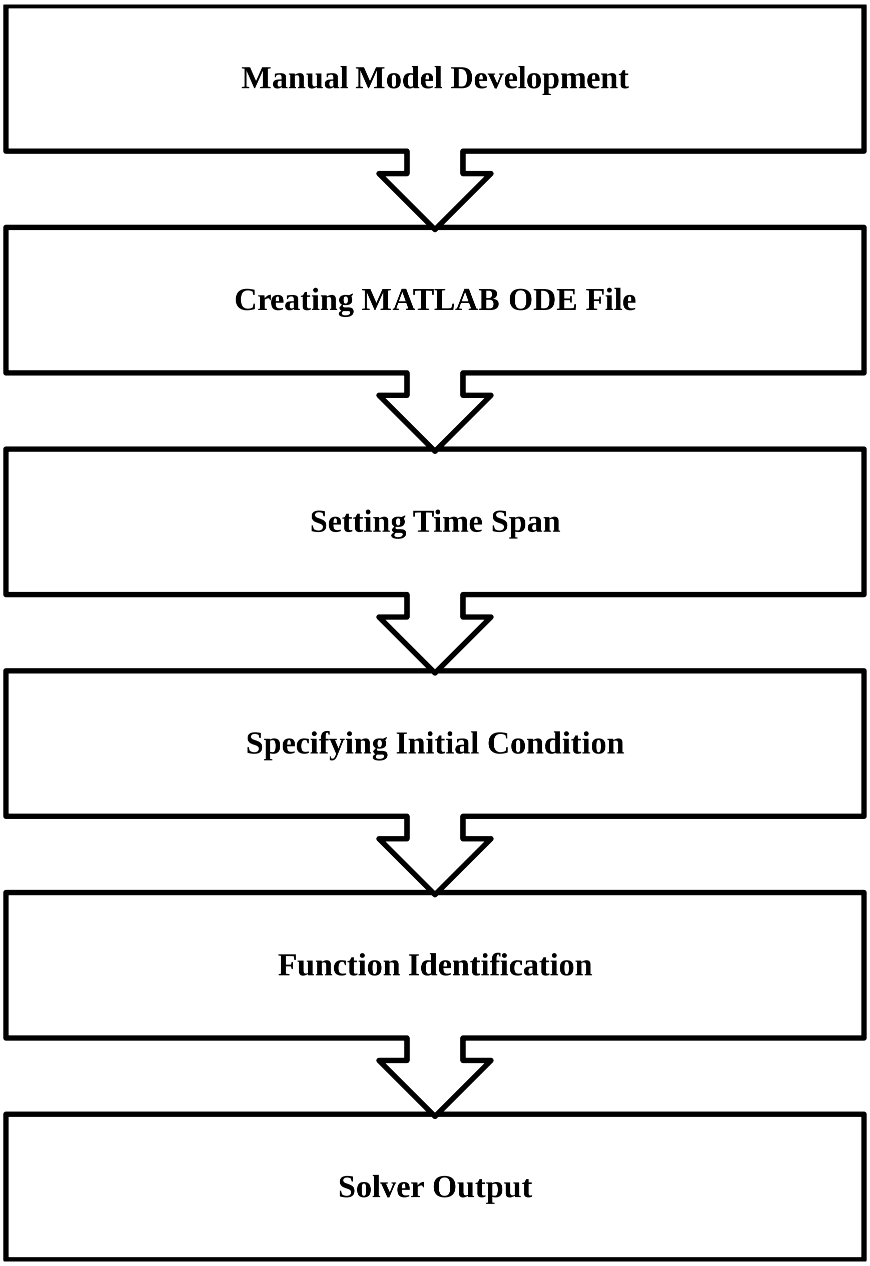


Figure 3.1 Flow Chart on MATLAB ODE Solving Procedure

3.2 Free Radical Polymerization Kinetic Mechanism

Kinetic mechanism of the free radical polymerization (equation 1 to 7) was shown as below (Baillagou and Soong, 1985; Ray, 1972 and Tirrell et al., 1987):

Initiation:

$$I \xrightarrow{k_i} 2\dot{I} \tag{1}$$

$$\dot{I} + M \xrightarrow{k_{Io}} P_1 \tag{2}$$

Propagation:

$$P_n + M \xrightarrow{k_p} P_{n+1} \tag{3}$$

Termination by coupling and disproportionation reaction:

$$P_n + P_m \xrightarrow{k_{tc}} D_{n+m} \tag{4}$$

$$P_n + P_m \xrightarrow{k_{td}} D_n + D_m \tag{5}$$

Chain transfer to monomer:

$$P_n + M \xrightarrow{k_{fm}} D_n + P_1 \tag{6}$$

Chain transfer to solvent:

$$P_n + S \xrightarrow{k_{fs}} D_n + P_1 \tag{7}$$

3.3 Mathematical Model Development

A mathematic model was the crucial part in optimization problem solving because type of problem solving tool was dependent on type of problems. Since the problem in this study was in the form of ordinary differential equations, therefore, ODE solver was the optimal solving tool. Optimization in batch system consisted of two dynamics which were reactor and jacket dynamics. Gel effect and glass effect were considered in the polymerization models. The important variables involved were monomer conversion, monomer concentration, initiator concentration, reactor temperature and jacket temperature. The detail mathematical models were presented as following.

3.3.1 Assumptions on Solution Polymerization of MMA

Some assumptions for the solution polymerization process of MMA were made in this study (Soroush and Kravaris, 1992).

i. All of the reaction steps were elementary and irreversible.
ii. Initiator efficiency was assumed remains constant along the process.
iii. The rates of the reaction steps were independent of the live polymer chain length.
iv. The rates of chain transfer to solvent reactions were negligible compared to the other reactions.
v. Overall heat transfer coefficient keeps in constant during the polymerization.

3.3.2 Reactor Dynamic

Rates of reactants consumption for initiation (8) and propagation (9) (Baillagou and Soong, 1985) and (Ray, 1972):

$$R_i = -k_i C_i \tag{8}$$

$$R_m = -C_m \xi_o (k_p + k_{fm}) \tag{9}$$

Live polymer chains (10):

$$\xi_o = \left(\frac{2f k_i C_i}{k_t}\right)\text{^}0.5 \tag{10}$$

Gel and glass effect models (11 to 13) (Chiu et al., 1983):

$$k_t = \frac{k_{to}}{1+\frac{\xi_o^2 \mathrm{k_{to}}}{D k_{\theta t}}} \tag{11}$$

$$k_p = \frac{k_{po}}{1+\frac{\xi_o \mathrm{k_{po}}}{D k_{\theta p}}} \tag{12}$$

$$D = exp\left(\frac{2.3(1-\Phi_p)}{A(T)+B(T-\Phi_p)}\right) \tag{13}$$

A was a function of reactor and glass transition temperatures (14) and B was a constant:

$$A = 0.168 - 8.21x10^{-6}(T - T_{gp})^2 \tag{14}$$

Arrhenius Law for termination, propagation, initiation and chain transfer to monomer are shown as following (15 to 20):

$$k_{to} = Z_{to}\, exp\left(\frac{-E_{to}}{RT}\right) \tag{15}$$

$$k_{po} = Z_{po}\, exp\left(\frac{-E_{po}}{RT}\right) \tag{16}$$

$$k_{\theta t} = C_i(0) Z_{\theta t}\, exp\left(\frac{-E_{\theta t}}{RT}\right) \tag{17}$$

$$k_{\theta p} = Z_{\theta p}\, exp\left(\frac{-E_{\theta p}}{RT}\right) \tag{18}$$

$$k_{fm} = Z_{fm}\, exp(\frac{-E_{fm}}{RT}) \tag{19}$$

$$k_i = Z_i\, exp\left(\frac{-E_i}{RT}\right) \tag{20}$$

Volume fraction of polymer (21 to 23):

$$\Phi_p = \frac{\frac{\mu_1}{\rho_p}}{\frac{\mu_1}{\rho_p}+\frac{C_m M_m}{\rho_m}+\frac{C_s M_s}{\rho_s}} \tag{21}$$

$$C_s = C_{so}(\frac{1+\varepsilon\frac{C_m}{C_{mo}}}{1+\varepsilon}) \tag{22}$$

$$\mu_1 = \frac{M_m}{1+\varepsilon}(C_{mo} - C_m) \tag{23}$$

During process from converting monomer to polymer, density increased, thus, the effect of volume change with conversion was considered in modeling the reactor (Schmidt and Ray, 1981; Hamer et al., 1981; Baillagou and Soong, 1985 and Tirrell et al., 1987). Volume decreased as the conversion increased. The formula of volume change was (24):

$$V = V_o(1 + \varepsilon x_m) \tag{24}$$

Volume expansion factor (25 and 26):

$$\varepsilon = \Phi_{mo}(\frac{\rho_m}{\rho_p} - 1) \tag{25}$$

$$\Phi_{mo} = C_{mo} M_m / \rho_m \tag{26}$$

Fractional monomer conversion (27):

$$x_m = \frac{C_{mo}V_o - C_m V}{C_{mo}V_o} = \frac{1-\frac{C_m}{C_{mo}}}{1+\varepsilon\frac{C_m}{C_{mo}}} \tag{27}$$

Species balance for monomer concentration (28a), initiator concentration (29a), reactor temperature (30a) and process parameter (31):

$$\frac{dC_m}{dt} = \left(1 + \varepsilon\frac{C_m}{C_{mo}}\right) R_m \tag{28a}$$

$$\frac{dC_i}{dt} = R_i + \varepsilon\frac{C_i}{C_{mo}} R_m \tag{29a}$$

$$\frac{dT}{dt} = \frac{\alpha_o k_p\ \xi_o C_m}{1+\varepsilon\frac{C_m}{C_{mo}}} + \alpha_1(T_j - T) \tag{30a}$$

$$\alpha_o = \frac{(-\Delta H_p)V_o(1+\varepsilon)}{mC} \tag{31}$$

3.3.3 Jacket Dynamic

Heat balance for the jacket (32a):

$$\frac{dT_j}{dt} = \alpha_2(T - T_j) + \alpha_3(T_\infty - T_j) + \alpha_4(F_{cw}\rho_w C_w(T_{cw} - T_j) + P) \tag{32a}$$

In order to use the two manipulated variables (P and F_{cw}) in the control law, both variables was combined to obtain a single manipulated variable (Jutan and Uppal, 1984). Overall rate of the heat addition (33):

$$\hat{u} = P - F_{cw}C_w\rho_w(T_j - T_{cw}) \tag{33}$$

3.3.4 Overall Dynamic Model

The overall dynamic model for the reactor and jacket (28b, 29b, 30b, 32b and 34) were shown as following and the derivation equation of monomer conversion was attached in Appendix A.

$$\frac{dC_m}{dt} = f_1\,(C_m, C_i, T) \tag{28b}$$

$$\frac{dC_i}{dt} = f_2\,(C_m, C_i, T) \tag{29b}$$

$$\frac{dT}{dt} = \frac{\alpha_o k_p\, \varepsilon_o C_m}{1+\varepsilon \frac{C_m}{C_{mo}}} + \alpha_1(T_j - T) \tag{30b}$$

$$\frac{dT_j}{dt} = \alpha_2\left(T - T_j\right) + \alpha_3\left(T_\infty - T_j\right) + \alpha_4 \hat{u} \tag{32b}$$

$$\frac{dx_m}{dt} = -R_m\left(\frac{1+\varepsilon x_m}{C_{m0}+\varepsilon C_m}\right)\left(1+\varepsilon\frac{C_m}{C_{m0}}\right) \tag{34}$$

3.3.5 Experimental Parameter

Table 3.1 below listed out the parameters used in both reactor and jacket dynamics models of polymerization optimization (Baillagou and Soong, 1985).

Table 3.1 Parameter in Polymerization Optimization Model

Parameter	Value	Unit
B	0.03	-
Z_{to}	$9.8000\text{x}10^{7}$	$m^3\,kgmole^{-1}s^{-1}$
E_{to}	$2.9442\text{x}10^{3}$	$kJ\,kgmole^{-1}$
Z_{Po}	$4.9167\text{x}10^{5}$	$m^3\,kgmole^{-1}s^{-1}$
E_{Po}	$1.8283\text{x}10^{4}$	$kJ\,kgmole^{-1}$
$Z_{\Theta t}$	$1.4540\text{x}10^{20}$	s^{-1}
$E_{\Theta t}$	$1.4584\text{x}10^{5}$	$kJ\,kgmole^{-1}$
$Z_{\Theta p}$	$3.0233\text{x}10^{13}$	s^{-1}
$E_{\Theta p}$	$1.1700\text{x}10^{5}$	$kJ\,kgmole^{-1}$

Table 3.1. Continued

Parameter	**Value**	**Unit**
ρ_m	915.1	kg m^{-3}
ρ_s	842	kg m^{-3}
ρ_p	1200	kg m^{-3}
M_m	100.12	kg kgmole^{-1}
M_s	921.4	kg kgmole^{-1}
T_{gp}	387.2	K
$(-\Delta H_p)$	5.78x10^{4}	kJ kgmole^{-1}
Z_{fm}	4.6610x10^{9}	m^{3} kgmole^{-1}s^{-1}
E_{fm}	7.4479x10^{4}	kJ kgmole^{-1}
Z_i	2.5933x10^{15}	s^{-1}
E_i	1.2877x10^{5}	kJ kgmole^{-1}
C	2.2	kJ kg^{-1} K^{-1}
f	0.58	-
T_{cw}	279.8	K
T_∞	293.2	K
m	1.257	kg
C_w	4.2	kJ kg^{-1}K^{-1}
$C_i(0)$	0.13	kgmole^{-3}
$C_m(0)$	6.01	kgmole^{-3}
P	0.65	kJ/s
F_{cw}	2.555x10^{-6}	m^{3}/s
α_1	0.0038	-
α_2	0.0008	-
α_3	0.00037	-
α_4	0.0664	-
C_{S0}	8.547	kgmole m^{-3}
V_o	1.5x10^{-3}	m^{3}
Φ_{S0}	0.3	-
R	8.314	kJ kg mole^{-1} K^{-1}

3.3.6 Analysis of Degree of Freedom (DOF)

Number of equations = 27

$$\{\, R_i\ ;\ R_m\ ;\ k_i\ ;\ C_i\ ;\ C_m\ ;\ \varepsilon_o\ ;\ k_p\ ;\ k_{fm}\ ;\ \xi_o\ ;\ f\ ;\ k_t\ ;\ k_{to}\ ;\ k_{\theta t}\ ;\ D\ ;\ k_{po}\ ;\ k_{\theta p}\ ;$$

$$A\ ;\ B\ ;\ \Phi_p\ ;\ T\ ;\ T_{gp}\ ;\ T_j\ ;\ C_s\ ;\ C_{so}\ ;\ \mu_1\ ;\ \varepsilon\ ;\ V\ ;\ x_m\ ;\ \Phi_{mo}\ ;\ \alpha_o\ ;\ C_{mo}\ ;\ V_o\ ;\ \alpha_1\ ;$$

$$R\ ;\ Z_{to}\ ;\ E_{to}\ ;\ Z_{po}\ ;\ E_{po}\ ;\ Z_{\theta t}\ ;\ E_{\theta t}\ ;\ Z_{\theta p}\ ;\ E_{\theta p}\ ;\ Z_{fm}\ ;\ E_{fm}\ ;\ Z_i\ ;\ E_i\ ;\ \rho_p\ ;\ M_m\ ;$$

$$\rho_m\ ;\ M_s\ ;\ \rho_s\ ;\ \Delta H_p\ ;\ m\ ;\ C\ ;\ \alpha_2\ ;\ \alpha_3\ ;\ \alpha_4\ ;\ T_\infty\ ;\ F_{cw}\ ;\ \rho_w\ ;\ C_w\ ;\ T_{cw}\ ;\ P\ ;\ \hat{u}\,\}$$

Number of variables = 65

Number of known parameters = 38   (Refer to Table 3.1)

DOF = Number of variables–Number of equations–Number of parameters

= 65-27-38

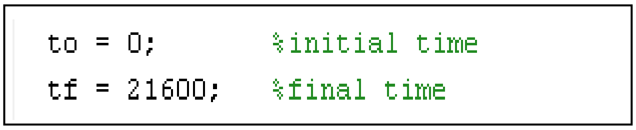
= 0

3.4 Creating MATLAB ODE File

MATLAB ODE file sometime also can be called as M-file. An ODE file always involved at least two arguments which were “*t*” and “*y*”. “*t*” argument representing independent variable while “*y*” argument representing the dependent variable. Sometime it can be defined as the rate of “*y*”. In this study, “PSM_MMA.m” was the M-file for both simulation and optimization of MMA solution polymerization. The m-file was attached in Appendix B.

3.5 Setting Time Span

Time span was a vector of time values used to determine a problem. General form of time span was [*t0, tfinal*] which t0 was the initial time (normally was started with zero time) and tfinal was the end of time. Solver will be integrated the problems from *t0* (initial) to tfinal (end). The time values must be in order, either all increasing or decreasing. Command for time span in MATLAB was in the unit of second. Since the duration time in this study was set 6 hours (21600s), therefore the command was in the form of [0 21600]. Another type of command was shown in Figure 3.2.

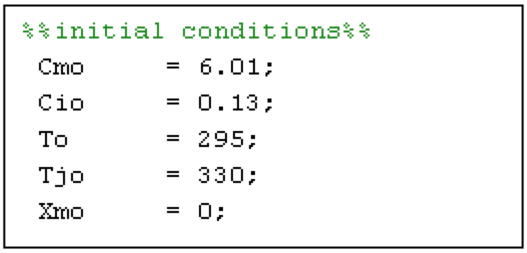


```
to = 0;        %initial time
tf = 21600;    %final time
```

Figure 3.2 Command for Setting Time Span

3.6 Specifying Initial Condition

In this study, initial condition of the variables was known. At initial time, concentration of monomer was 6.01kgmole m^{-3}, concentration of initiator was 0.13kgmole m^{-3}, reactor temperature was 295K, jacket temperature was 330K and the conversion of monomer was zero since there was no reaction between monomer and other reactants at the beginning. The initial condition was shown in Figure 3.3.



```
%%initial conditions%%
 Cmo      = 6.01;
 Cio      = 0.13;
 To       = 295;
 Tjo      = 330;
 Xmo      = 0;
```

Figure 3.3 Initial Condition in Solution Polymerization

3.7 Function Identification

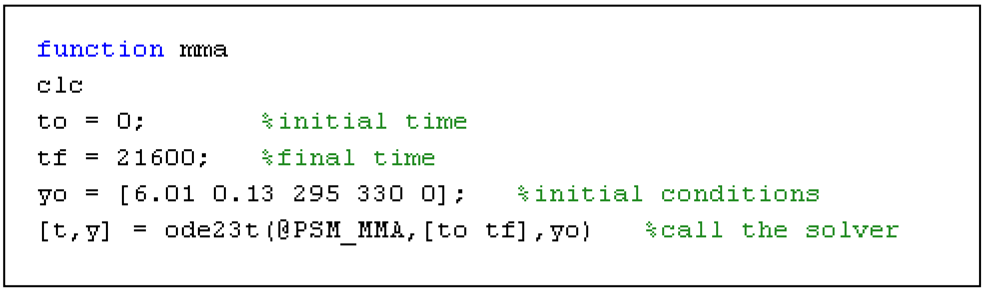
Once the ODE system was coded in an ODE file, the MATLAB ODE solver can be applied to solve the problems in the given time interval with an initial condition. The general function for the ODE solvers was normally in the form. Figure 3.4 was the function command for ode23t and Figure 3.5 shows the functions involved in this study.

[*t*,*y*] = *solver* (@Function, timespan, initial values)

>> tspan = [0 21600] ;   *%Integration range*

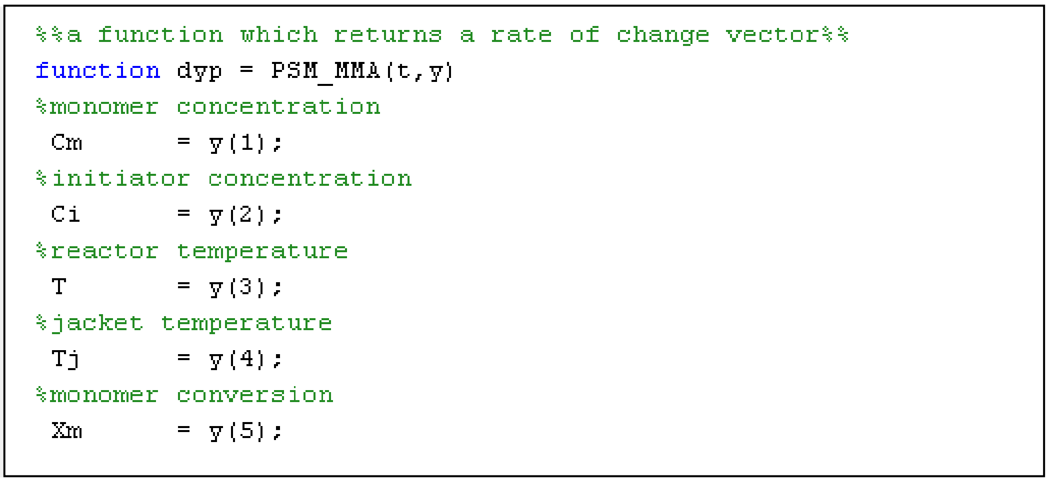
>> *y0* = [6.01 0.13 295 330 0];   *%Initial condition*

>> [*t*,*y*] = ode23t (@PSM_MMA, tspan, *y0*);   *%MATLAB function*



```
function mma
clc
to = 0;        %initial time
tf = 21600;    %final time
yo = [6.01 0.13 295 330 0];    %initial conditions
[t,y] = ode23t(@PSM_MMA,[to tf],yo)    %call the solver
```

Figure 3.4 Function Command for ode23t



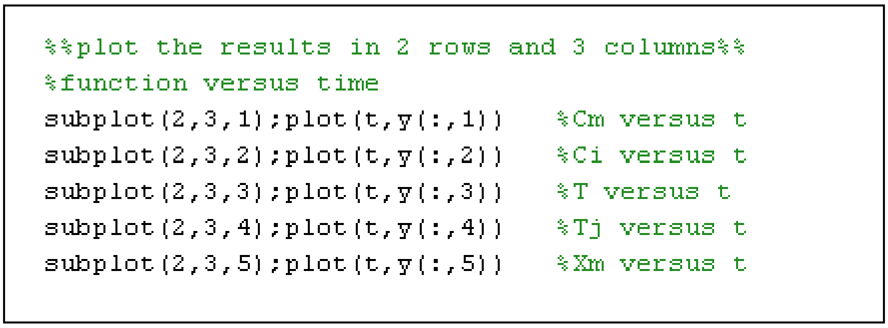
```
%%a function which returns a rate of change vector%%
function dyp = PSM_MMA(t,y)
%monomer concentration
 Cm       = y(1);
%initiator concentration
 Ci       = y(2);
%reactor temperature
 T        = y(3);
%jacket temperature
 Tj       = y(4);
%monomer conversion
 Xm       = y(5);
```

Figure 3.5 Five Dependent Functions in Solution Polymerization of MMA

3.8 Solver Output

After the problems have been solved, plot command was used to view the solver output. The solver output was represented by graphical results. The common plot command for one graph was shown as following while Figure 3.6 shows the plot command for few graphs plotted at the same time.

```
>>plot(t,y(:,1));                                   %Curve pattern
>>title(‘Title of the graph’);
>>xlabel(‘independent variable’);
>>ylabel(‘dependent variable’);
```



```
%%plot the results in 2 rows and 3 columns%%
%function versus time
subplot(2,3,1);plot(t,y(:,1))    %Cm versus t
subplot(2,3,2);plot(t,y(:,2))    %Ci versus t
subplot(2,3,3);plot(t,y(:,3))    %T versus t
subplot(2,3,4);plot(t,y(:,4))    %Tj versus t
subplot(2,3,5);plot(t,y(:,5))    %Xm versus t
```

Figure 3.6 Plot Command for Five graphs

CHAPTER 4

RESULT AND DISCUSSION

4.1 Optimization using ODE23t by MATLAB

The primary objective of this study was to obtain the optimum operation condition (reactor temperature, jacket temperature and concentration of initiator) for solution polymerization of MMA in batch reactor in order to get the best performance and product. This section was included the results obtained from the ordinary differential equation optimization by MATLAB software. Results were illustrated in graphically. Based on the results, the changes in each parameter were discussed. Finally, the result obtained from MATLAB in this study was compared to the experimental result from the previous research by Soroush and Kravaris (1992).

4.1.1 Case Study 1: Effect of Initiator Concentration

4.1.1.1 Formulation of Optimization Problem

Objective of the case study 1 was to obtain optimum initial concentration of initiator (C_{i0}) in order to get the maximum conversion of monomer (X_m) in minimum batch time (t_f^*). Reactor temperature (T), jacket temperature (T_j) and concentration of monomer (C_{m0}) were constant.

Max X_m

Min t_f^*

C_{i0}

s.t. $f(t, X_m(t)) = 0, [t_0, t_f]$ model equation

$t_f = 21600$

$T = 300$

$T_j = 335$

$C_{m0} = 6.01$

$0.05 < C_{i0} < 0.30$

4.1.1.2 Result and Discussion

The result for the optimization of initial concentration of initiator at constant reactor and jacket temperature was shown in Table 4.1.

Table 4.1 Result for Optimization of Initiator Concentration

C_i	X_m	t_f^*
0.05	0.69	21364
0.10	0.82	21243
0.13	0.86	21276
0.14	0.88	21580
0.15	0.89	21540
0.20	0.93	21022
0.21	0.94	20450
0.22	0.95	20647
0.23	0.96	20448
0.24	0.98	20239
0.25	0.97	20523
0.26	0.93	19287
0.27	0.90	16681
0.28	0.89	12666
0.29	0.88	10459
0.30	0.87	10098

Conversion of monomer was depended on concentration of initiator. In the optimization section, when the initial concentration of initiator added into the reactor was less than 0.24 kgmole m^{-3}, conversion of monomer was in the range of 0.69 to 0.96 which long batch time was taken. The maximum conversion of 0.98 was reached when the initial concentration of initiator was 0.24 kgmole m^{-3}. However, conversion was started to be decreased when initial concentration was more than 0.25 kgmole m^{-3}. Thus, the optimum initial concentration of AIBN was at 0.24 kgmole m^{-3}.

Since there was sufficient amount of initiator was added into reactor, the reaction between initiator with monomer was great as well as the propagation rate. Therefore, concentration of initiator was dramatically decreased from 0.24 to 0.172 kgmole m^{-3} at the first 2400s which was shown in Figure 4.1. After 2400s, amount of remaining initiator was limited. Due to the large amount of long chain occupied large space, the probability of initiator to move and reacted with monomer was reduced.

Thus, the rate of propagation was just increased slightly and the concentration of initiator was decreased slowly towards time.

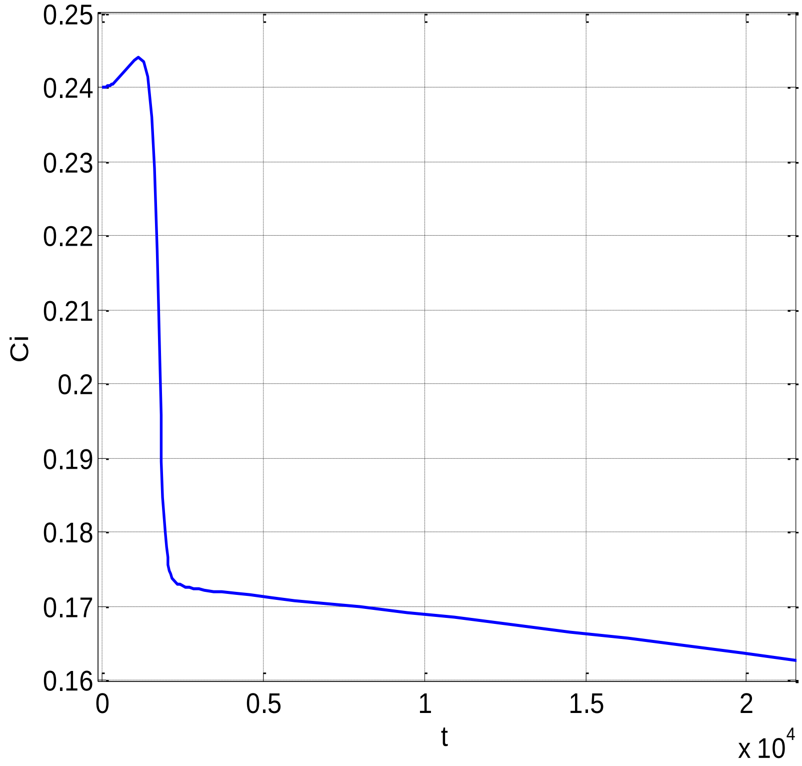


Figure 4.1 Concentration of Initiator (kgmole m^{-3}) versus Time (s)

4.1.2 Case Study 2: Effect of Reactor Temperature

4.1.2.1 Formulation of Optimization Problem

Objective of this second case study was to optimize the reactor temperature (T) to obtain a maximum conversion of monomer (X_m) in the minimum batch time (t_f^*). The constant variable in this case study was jacket temperature (T_j), initial concentration of initiator (C_{i0}) and initial concentration of monomer (C_{m0}).

Max X_m

Min t_f^*

T

s.t. $f\,(t, X_m(t)) = 0,\ [t_0, t_f]$ model equation

$t = 21600$

$T_j = 335$

$C_{m0} = 6.01$

$C_{i0} = 0.24$

$295 < T < 340$

4.1.2.2 Result and Discussion

Table 4.2 shows the optimization result for reactor temperature at constant initial concentration of initiator and jacket temperature.

Table 4.2 Result for Optimization of Reactor Temperature

T	X_m	t_f^*
295	0.96	20450
296	0.97	21452
297	0.97	21000
298	0.97	20788
299	0.97	18389
300	0.98	20239
301	0.98	21064
302	0.98	20713
303	0.98	20580
304	0.97	17960
305	0.96	14406
310	0.91	12684
315	0.87	12190
320	0.84	10271

Table 4.2. Continued

T	X_m	t_f^*
325	0.83	10410
330	0.84	9524
335	0.76	9190
340	0.71	8794

Temperature gave significance effect on initiator decomposition and monomer conversion. Monomer conversion was increased as temperature increased (295 to 300K). Sufficient high temperature was important because this can reduce the gel effect which the amplitude of gel effect was diminished. Based on the optimization result in Table 4.2, monomer conversion was started to be decreased at very high temperature (304 to 340K). An optimum initial temperature at 300K was set to obtained high conversion with 0.98 in the minimum batch time.

Figure 4.2 shows that there was a fluctuation in reactor temperature. The unstable reactor temperature was suddenly increased from 300K to maximum 368K at the first 2400s due to the large amount of heat released (exothermic) from the reaction between monomer and initiator. After certain time, there was limiting for propagation reaction due to limited amount of both remained monomer and initiator. Temperature did not been changed significance and maintained close to 324K. Besides that, solvent (toluene) was acted to absorb the heat to decrease the temperature otherwise than reduce the viscosity of medium. Jacket was used to control the reactor temperature to avoid increased to too high.

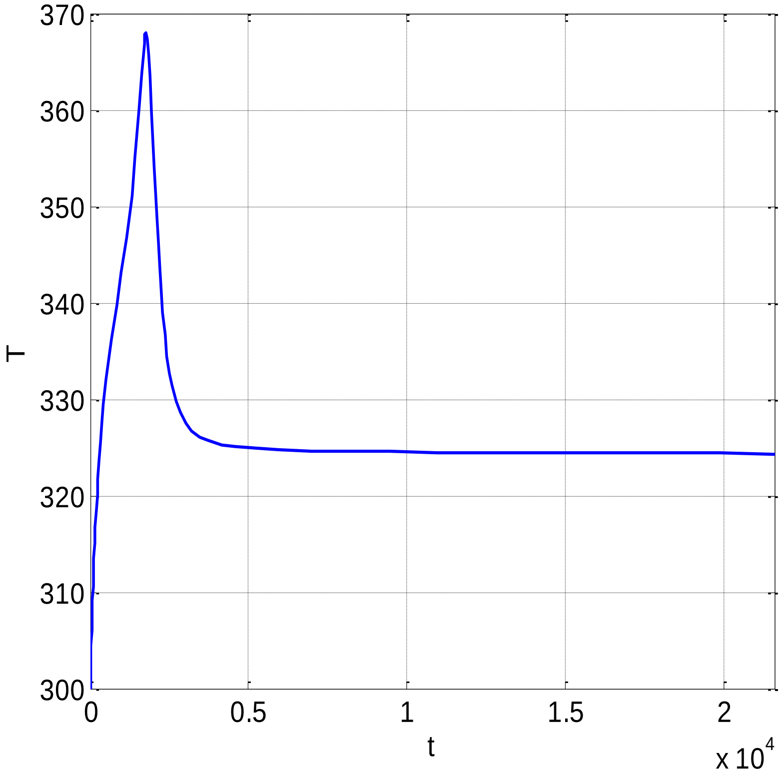


Figure 4.2 Reactor Temperature (K) versus Time (s)

4.1.3 Case Study 3: Effect of Jacket Temperature

4.1.3.1 Formulation of Optimization Problem

This case study was to obtain maximum conversion of monomer (X_m) in minimum batch time (t_f^*) by manipulated the jacket temperature (T_j). In this optimization, reactor temperature (T), initial concentration of initiator (C_{i0}) and initial concentration of monomer (C_{m0}).

Max X_m

Min t_f^*

T_j

s.t. $f(t, X_m(t)) = 0, [t_0, t_f]$ model equation

$t = 21600$

$T = 300$

$C_{m0} = 6.01$

$C_{i0} = 0.24$

$290 < T_j < 355$

4.1.3.2 Result and Discussion

The result for the optimization of jacket temperature at constant reactor temperature and initial concentration of initiator was listed out in Table 4.3.

Table 4.3 Result for Optimization of Jacket Temperature

T_j	X_m	t_f^*
290	0.91	21334
295	0.91	21167
300	0.91	20911
310	0.92	21377
320	0.93	21334
330	0.94	20785
331	0.94	20457
332	0.95	21321
333	0.95	20886
334	0.96	21071
335	0.98	20239
336	0.93	10620
337	0.88	10026
338	0.85	8015

Table 4.3. Continued

T_j	X_m	t_f^*
339	0.82	7719
340	0.82	14951
345	0.69	20867
350	0.74	21000
355	0.64	19349

Jacket temperature was used to control the reactor temperature and avoid too much heat release to the surrounding which thermal runaway may occurs. Through the optimization by MATLAB, jacket temperature was optimum at 335K where a highest conversion at 0.98 was achieved. Low conversion of monomer was obtained at jacket temperature lower than 335K and the conversion was started to be decreased constantly at temperature higher than 345K.

At the first 4000s, jacket temperature was decreased from 335K to 325K in order to minimize the temperature raise and thermal runaway of reaction in reactor by absorbed the heat released. After certain time, amount of reactants was become less and the rate of propagation was started to be slow down due to the weak reaction between both initiator and monomer. Since there was a slow reaction between reactants, amount of heat released was become less and the temperature profile became less fluctuating. Once jacket temperature meet the same point with the reactor temperature, both temperatures were stable and maintained at about 324K. Figure 4.3 shows the jacket temperature as the function of time.

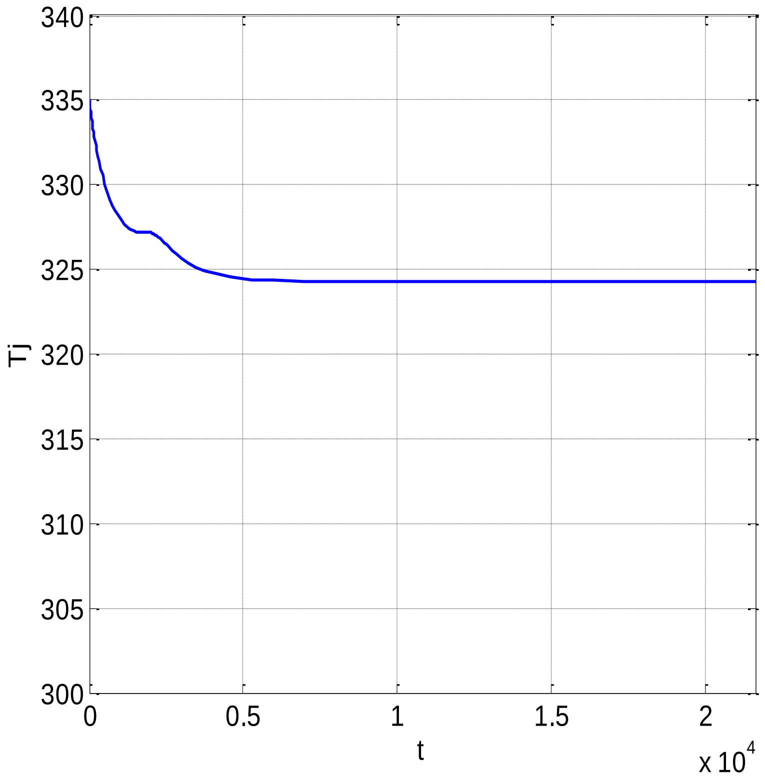


Figure 4.3 Jacket Temperature (K) versus Time (s)

4.1.4 Conversion of Monomer

High inlet temperature of reactor rapidly increased the decomposition of initiator as well as increased in propagation rate. This leads to dramatically increased in conversion of monomer at the first 2400s. Since high consumption amount of initiator and monomer was needed to achieve high conversion (X_m = 0.88) at the beginning, thus, there was limited amount of both initiator and monomer remained in the system. Due to this condition, polymerization became slowly and takes long periods of time to achieve the maximum conversion (X_m = 0.98). At the optimum process conditions, the solution polymerization of MMA takes 20239s (5.6 hours) to reach the maximum conversion which was less than the original process duration, 21600s (6 hours). This shows that MATLAB can solve the optimization problem effectively and economically.

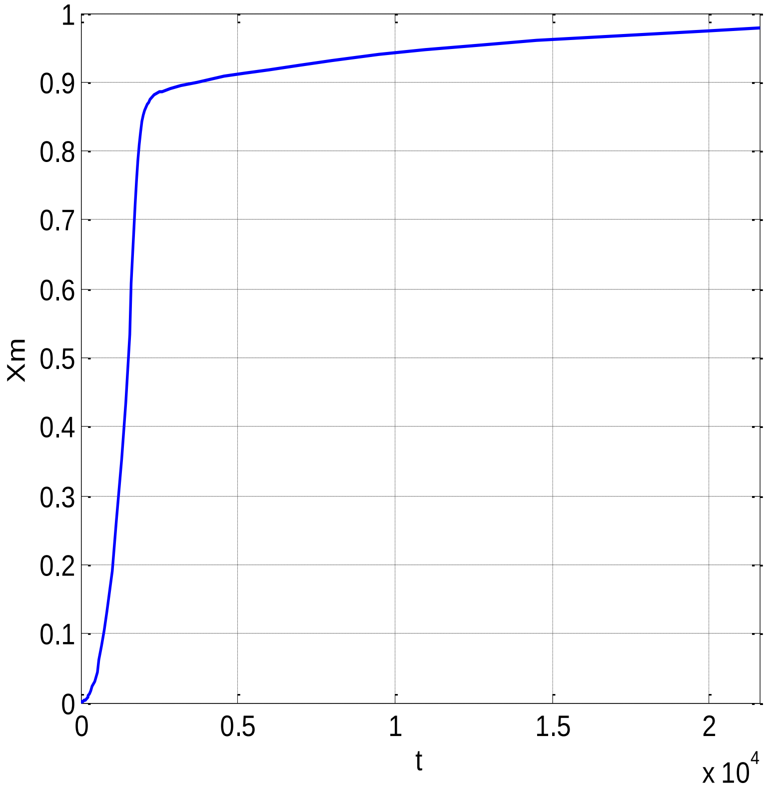


Figure 4.4 Conversion of Monomer versus Time (s)

4.1.5 Concentration of Monomer

In this study, concentration of monomer was a constant variable (limiting reactant) but not as manipulated variable. 6.01 kgmole m^{-3} of MMA was fed to the batch reactor at the beginning accompany with AIBN and toluene. At the first 2400s, high monomer consumption rate was obtained which means that concentration of monomer was decreased dramatically from 6.01 kgmole m^{-3} to 0.8 kgmole m^{-3}. This was because of the vigorous reaction between monomer and initiator to produce polymer. This result in the high conversion of monomer showed in previous Figure 4.4. Due to the limited amount of initiator and monomer remained in the reactor, the reaction became slowly and constantly after first 2400s to the end of process. Thus, monomer conversion was significance depended on the concentration of monomer.

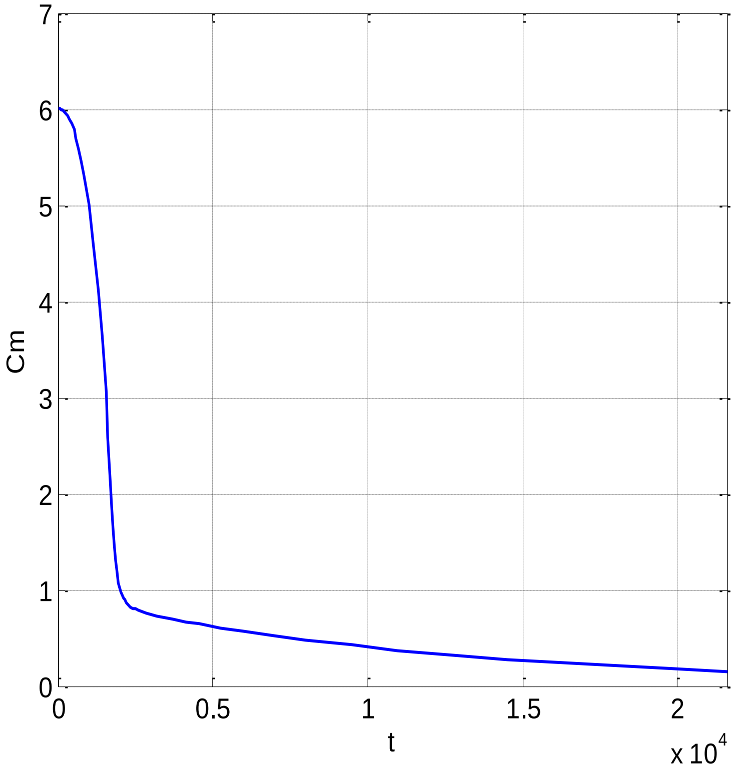


Figure 4.5 Concentration of Monomer (kgmole m^{-3}) versus Time (s)

4.1.6 Summary of Optimization Result

The overall observations from the graphical results (Figure 4.1 to Figure 4.5) were summarized in Table 4.4.

Table 4.4 Summary of Optimization Result

Duration (sec)	Parameter	Observation of Result
0 to 2400	C_i	• Concentration of initiator decreased dramatically by 28.3% of initial concentration
	T	• Suddenly increased from 300K to 368K but then decreased to 325K
	T_j	• Decreased from 335K to 327K
	X_m	• Increased rapidly to 88% of conversion
	C_m	• Decreased rapidly by 86.7% of initial concentration
2400 to 21600	C_i	• Decreased slowly by 5.2% from 0.172 to 0.163kgmole m^{-3}
	T	• Constant at 324K
	T_j	• Decreased slightly from 327K to 325K, then constant along 324K
	X_m	• Increased slowly and constantly from 0.88 to 0.98
	C_m	• Constantly and slowly decreased

4.2 Simulation: Comparison between this Study and Previous Research

Simulation was a useful tool to explain the behavior of an operation for a system or model. By using the reactor and jacket dynamic models from the previous research, simulation of solution polymerization of MMA was done by using ode23t in MATLAB. The result in this study was compared with the experimental result from previous research by Soroush and Kravaris (1992).

4.2.1 Reactor Temperature

Figure 4.6 shows that reactor temperature in this study kept in higher than the temperature in original research. One of the factors was the heat lost from the system to surrounding. For the simulation in this study, amount of initiator reacted with monomer was increased as well as the propagation rate. This caused highly exothermic reaction in the reactor and thus outlet temperature of the reactor increased too. Therefore, when there was a dramatically increased in conversion of monomer, the temperature will increased significance too. Standard deviation between the results of this study and the previous research by Soroush and Kravaris (1992) was 5.96.

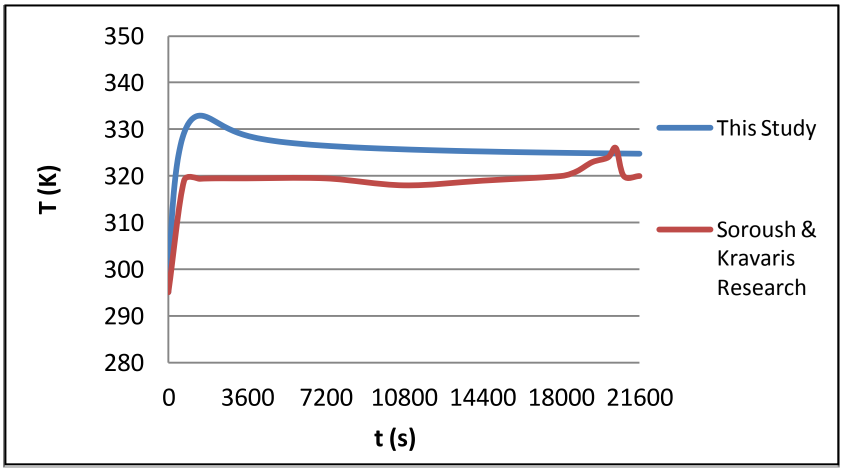


Figure 4.6 Comparison Result for Reactor Temperature

4.2.2 Jacket Temperature

From the Figure 4.7, jacket temperature in this study was observed to be decreased slightly but the jacket temperature for previous research was more fluctuating. Jacket temperature in real experimental work can be affected by environmental condition. This showed that the operation condition controlled under software was more stable than the manual experimental work. Standard deviation between the results of this study and the previous research by Soroush and Kravaris (1992) was 7.26.

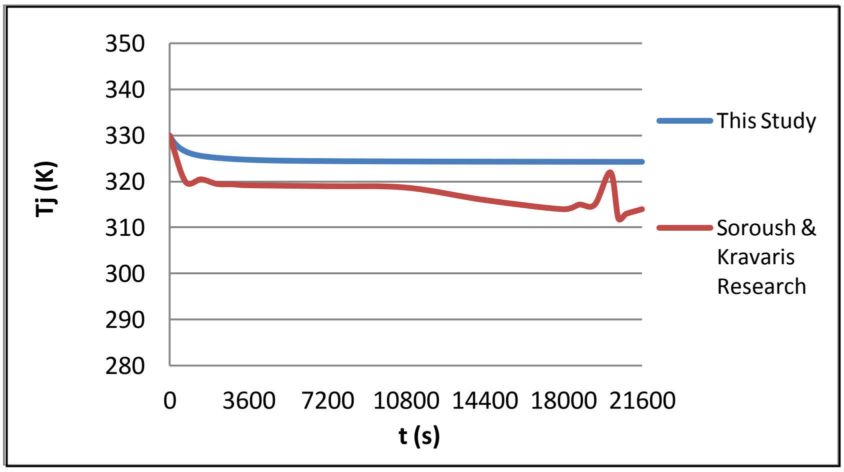


Figure 4.7 Comparison Result for Jacket Temperature

4.2.3 Conversion of Monomer

Compared to both results in reactor and jacket temperature simulation, monomer conversion for two different studies showed a quite large deviation which shown in Figure 4.8. The standard deviation between the results in this study and the previous research by Soroush and Kravaris (1992) was 0.24. This means that the monomer conversion in this study was higher than the previous research by average value of 0.24. However, at 19000s (5.3 hours), the monomer conversion for the previous research was better than from the study. In this study, large amount of initiator was consumed at the beginning and caused the amount of initiator remained in reactor was limited. Therefore, rate of propagation at 19000s was lower than the previous research.

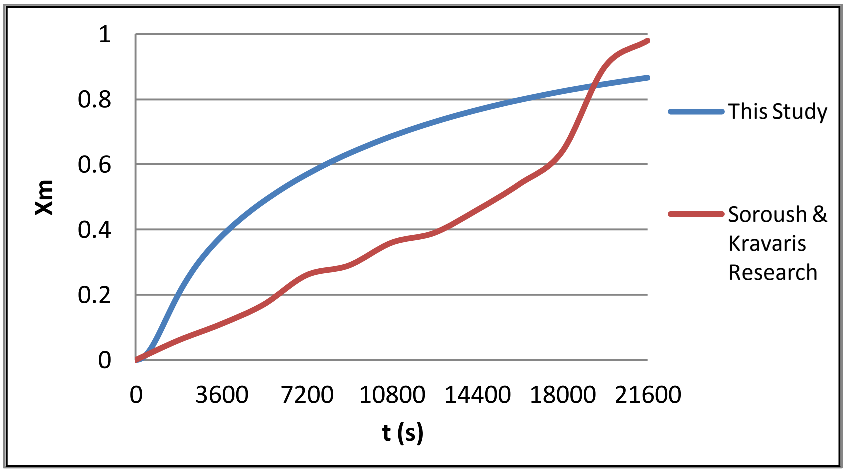


Figure 4.8 Comparison Result for Conversion of Monomer

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Introduction

In this study, the objectives were to develop the dynamic models, optimize the operating conditions of solution polymerization of MMA in batch reactor and compare the simulation results with the previous research by Soroush and Kravaris (1992). By conducting this study, the results outcomes had been discussed in the previous chapter. This chapter was to conclude the whole study based on the research finding. Recommendations were suggested in this section in order to improve the insufficient information in this study. Besides that, some suggestions gave a direction on future investigation.

5.2 Conclusion

In the simulation section, the dynamic model of solution polymerization was completely developed and simulated by using ode23t in MATLAB. The models involved were batch reactor and jacket dynamics models. The simulation by

MATLAB was feasible since the standard deviation between this study and the previous research by Soroush and Kravaris (1992) were acceptable.

Another objective where the optimization of operating condition was successful conducted. Solution polymerization of MMA achieved maximum conversion at 0.98 in the minimum batch time of 20239s (5.6 hours). The optimum initial concentration of initiator (AIBN) was 0.24kgmole m^{-3}. While 300K of initial reactor temperature and 335K of initial jacket temperature was obtained to achieve a high conversion of monomer.

In the conclusion, all objectives in this study were successful achieved. The ode23t solver was suitable to solve the moderately stiff problem in solution polymerization of MMA and MATLAB was a useful engineering problem solving tool which was effective and economical.

5.3 Recommendation

Other than the initial concentration of initiator (C_i), reactor temperature (T) and jacket temperature (T_j), some of others parameters can be optimized. The potential parameters are concentration of monomer (C_m), volume of solvent (V_{so}), input power (P) and cooling water flow rate (F_{cw}). Those parameters have impact on the conversion of monomer, molecular weight of polymer and the jacket temperature.

In this study, a constant value of 0.58 was used for the initiator efficiency. However, it was believed that the initiator efficiency (*f*) would not keep in constant in reality process. The initiator efficiency will decrease when the concentration of polymer chains was increase as well as the viscosity of medium in the batch reactor. Thus, it was recommended that a model for initiator efficiency will be developed to obtain more accurate results.

Since the concentration of polymer chains will increase in the process, thus viscosity of the reacting medium will increased too. This condition decreases the overall heat transfer coefficient (*U*) in the reactor. However, the overall heat transfer coefficient was assumed to be constant during the polymerization of MMA in order to make the problem easier to be solved. This may reduce the accuracy and effectiveness of the model. Thus, it was recommended that the heat transfer coefficient should be analyzed since it was variety with various temperatures.

REFERENCES

Angerer J, Kraemer A. (1996). Occupational chronic exposure to organic solvents. XVI. Ambient and biological monitoring of workers exposed to toluene. International Archives of Occupational and Environmental Health 69(2):91-6.

Baillagou, P. E. and D. S. Soong. (1985). “Major Factors Contributing to the Nonlinear Kinetics of Free-Radical Polymerization,’’ Chem. Eng. Sci., 40, 1, 75.

Baillagou P. E. and D. S. Soong. (1985). “Molecular Weight Distribution of Products of Free Radical Nonisothermal Polymerization with Gel Effect. Simulation for Polymerization of Poly(methyl methacrylate),’’ Chem. Eng. Sci., 40, 1, 87.

Barsky FC. (1976). In vitro microbial mutagenicity studies of 2,2’azobis (isobutyronitrile). Newark DE, USA: EI. DuPont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine.

Biondi M., Borzacchiello A. and Antonio Netti P. (2010). Isothermal and Non-isothermal Polymerization of Methyl Methacrylate in Presence of Multiple Initiators. Chemical Engineering Journal 162(2):776-786.

Budavari S, O'Neil MJ, Smith A and Heckelman PE. (1989). The Merck Index, 11th ed. Rahway, N.J.: Merck & Co., Inc.

Chapra, S.C. and R.P. Canale. (2006). Numerical Methods for Engineers. 5th Edition. McGraw Hill International Edition. ISBN: 007-124429-8.

CHEMFATE. (1994). Syracuse Research Corporation's Environmental Fate Data Base.

Cheng Z.P., X.L. Zhu, L.F. Zhang, N.C. Zhou and J.Y. Chen. (2006). Homogeneous Solution Reverse Atom Transfer Radical Polymerization of Methyl Methacrylate. Journal of Macromolecular Science, Part A: Pure and Applied Chemistry. 40(4):371-385.

Chiu, W. Y., G. M. Carratt and D. S. Soong. (1983). A Computer Model for the Gel Effect in Free-Radical Polymerization. Macromolecules, 16, 3, 348.

Clarkson, R. (2012). Advanced Organic Chemistry-Polymerisation. Chemistry Rule. Retrieved October 22, 2012 from http://www.chemistryrules.me.uk/candrands/polymerisation.htm

Cowie and John M. G. (1991). Polymers: chemistry and physics of modern material. Glasgow: Blackie. ISBN 0-412-03121-3.

Crowley T.J. and K.Y.Choi. (1996). On-line Monitoring and Control of a Batch Polymerization Reactor. Journal of Process Control. 6(2-3): 119-127.

Dixit M., S. Gupta, V. Mathur, K.S. Rathore, K. Sharma and N.S. Saxena. (2009). Study of Glass Transition Temperature of PMMA and Cds-PMMA Composite. Chalcogenide Letters. 6(3): 131-136.

Dormand, J. R. and P. J. Prince. (1980). A family of embedded Runge-Kutta formulae. J. Comp. Appl. Math., Vol. 6, pp 19-26.

Dormer. W., R. Gomes and M.E. Meek. (1998). Methyl Methacrylate. Concise International Chemical Assessment Document 4. World Health Organization, Geneva.

Duarte, F.J. (2009), Tunable Laser Applications. CRC, New York. Chapters 3 and 4

Ehrenstein, G.W. (2001). Polymeric Materials. Structure-Properties-Applications. Hanser Gardner Publications. ISBN: 3-446-21461-5.

Evonik Industries AG. (2011). GPS Safety Summary Methyl methacrylate. Technical Information. Version 2, pp 2/7.

Hahn. B.D. (2002). Essential MATLAB for scientists and engineers. 2nd Edition. Elsevier Butterworth Heinemann. ISBN: 0-7506-5240-3.

Harmer, J. W., T. A. Akramov and W. H. Ray. (1981). The Dynanic Behavior of Continuous Polymerization Reactors-II, Chem. Eng. Sci., 36, 1879.

Hawley G.G. (1981). The Condensed Chemical Dictionary, 10th ed. Van Nostrand Reinhold Co., New York.

Henini G., F. Souahi and Y. Laidani. (2012). Tracking Offline Conversion Solution Polymerization of Methyl Methacrylate/Vinyl Acetate in Toluene in a Reactor Calorimeter. Procedia Engineering. 33: 225-233.

HSDB. (1996). Hazardous Substances Data Bank. Tomes Vol 32, Micromedex, Inc

Hyung-Ju R, Yun-Jun H. and Hyun-Ku R. (1998). Application of adaptive model-predictive control to a batch MMA polymerization reactor. Chem. Eng. Sci., 53(21):3729-3739.

Ji, C. and Egolfopoulos F.N. (2011). Hydrogen Flame propagation of mixtures of air with binary liquid fuel mixtures. Proc. Comb. Inst. 33: 955–961. doi:10.1016/j.proci.2010.06.085

Gao, J, K. D. Hungenberg and A. Penlidis. (2004). Process Modelling and Optimization of Styrene Polymerization. Macromol. Symp. 206: 509-522.

Johannes K. F. (2005). Reactive Polymers Fundamentals and Applications: A Concise Guide to Industrial Polymers. Chemical Economic Handbook.

Jose, S. (2012). Methyl Methacrylate: A Global Strategic Business Report. Global Industry Analysts. Inc. (GIA). Retrieved April 30, 2012 from http://www.prweb.com/releases/methyl_methacrylate/polymethyl_methacrylate/prweb9382682.htm

Jutan, A. and A. Uppal. (1984). Combined Feedforward-Feedback Servo Control Scheme for an Exothermic Batch Reactor. Ind. Eng. Chem. Process Des. Res., 23, 597.

Keith L.H. and D.B. Walters. (1985). Compendium of Safety Data Sheets for Research and Industrial Chemicals. Part II. VCH Publishers, Deerfield Beach.

Key Centre for Polymer Colloids. (2001). Free radical polymerization. Australian Research Council's Research Centres Program. Retrieved October 25, 2012 from http://discovery.kcpc.usyd.edu.au/9.2.1-short/9.2.1_FRP.html

Kiparissides.C. (1996). Polymerization reactor modeling, a review of recent developments and future directions," Chemical Engineering Science, vol. 51, pp. 1637–1659.

Kutz and Myer. (2002). Handbook of Materials Selection. John Wiley & Sons. p. 341. ISBN 0-471-35924-6

Lepore R, A. Vande Wouwer, M. Remy, R. Findeisen, Z. Nagy and F. Allgower. (2007). "Optimization strategies for a MMA polymerization reactor." Computers & amp; Chemical Engineering 31(4): 281-291.

Lewis, Peter R, Reynolds, Ken, Gagg and Colin. (2004). Forensic materials engineering: case study. Boca Raton: CRC Press. ISBN 0-8493-1182-9

Mannsville. (1992). Toluene. Chemical Products Synopsis. Mannsville Chemical Products Corporation

Martin B. Hocking. (2005). Handbook of Chemical Technology and Pollution Control. Third Edition.

Merck Index. (1989). an Encyclopedia of Chemicals, Drugs, and Biologicals. 11th ed. Rahway, NJ07065, Merck & Co., Inc.: 11, 146

Merory and Joseph. (1968). Food Flavorings: Composition, Manufacture and Use. 2nd ed. Westport, CT: AVI Publishing Company, Inc.

Miller. (1996). Review of Orthopedics Fourth Edition. Philadelphia: W. B. Saunders. p. 129. ISBN 0-7216-5901-2

National Industrial Chemicals Notification and Assessment Scheme. (2009). Methyl Methacrylate (MMA) in Cosmetic Nail Preparations. NICNAS Existing Chemicals Information Sheet. Department of Health and Ageing.

Nexant Chem System. (2006). Methyl Methacrylate. Process Evaluation/Research Planning program. Retrieved 3 May, 2012 from http://www.chemsystems.com/reports/search/docs/abstracts/0405-2_abs.pdf

NIOSH. (1994). Pocket guide to chemical hazards. U.S. Department of Health and Human Services. DHHS(NIOSH) Publ. # 94-116 .

NITTO DENKO CORPORATION. Retrieved April 27, 2012 from http://www.nitto.com/rd/base/adhesive/composite.html

Philip, N. (2006). High-temperature radical polymerization of MMA in a continuous pilot scale process. Ecole Polytechnique Federale De Lausanne (EPFL).

Ray W. H. (1972). “On the Mathematical Modeling of Polymerization Reactors,” J. Macromolecules Sci.-Revs. Macromol. Chem., C8(1): 1-56.

Ray W. H. (1986). IEEE Control System Magazine, 6(4):3-8.

Richard T., Richard C.B., Wallace B.W. and Joseph A.S. (1998). Analysis, Synthesis, and Design of Chemical Processes. New Jersey: Prentice Hall PTR.

Schmidt, A. D. and W. H. Ray. (1981). The Dynamic Behavior of Continuous Polymerization Reactors-I. Chem. Eng. Sci.,36, 1401.

Semsarzadeh M. A., A. Karimi and M. Eshtad (1997). Polymerizations of Vinyl Acetate in Solution. Iranian Polymer Journal. 6(4).

Shampine, L.F. (1994). Numerical Solution of Ordinary Differential Equations. Chapman and Hall, New York.

Shampine, L.F. and M.K. Gordon. (1975). Computer Solution of Ordinary Differential Equations: the Initial Value Problem. W.H. Freeman, San Francisco.

Shampine, L.F. and M.W. Reichelt. (1997). The MATLAB Ode Suite. SIAM Journal on Scientific Computing. Vol. 18-1.

Shang, Y.R. and D. Kazmer. (2010). A MATLAB Program for Quantitative Simulation of Self-assembly of Polymer Blend Films with Nano-scaled Features. Center of high-rate Nano-manufacturing University of Massachusetts.

Simon,C.J. (n.d.). Plastics Business Data and Charts. Retrieved 7 October, 2012 from www.vke.de

Smiley RA. (1981). Nitriles. Kirk-Othmer encyclopedia of chemical technology 3rd ed. New York, USA: John Wiley and Sons, Inc. Vol 15: 888-909

Soroush M. and C. Kravaris. (1992). Nonlinear Control of a Batch Polymerization Reactor.AIChE Journal. Retrieved 15 March, 2012 from http://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=04791931

Koichi, N. and U. Toshiaki. (2004). Trends and Future of Monomer-MMA Technologies. SUMITOMO KAGAKU, vol. II. Sumitomo Chemical Co., Ltd.

Tirrell, M., R. Galvan and R. L. Laurence. (1987). Polymerization Reactors in Chemical Reaction and Reactor Engineering. J. 3. Carberry and A. Varma, eds., Marcel Dekker, Basel-New York.

Thomas, F.E., and David, M.H. (2001). Optimization of Chemical Processes 2nd e.d. New York: McGraw-Hill.

Tom Parker. (1999). Public Health Goal For Toluene In Drinking Water. California: Environmental Protection Agency, Office of Environmental Health Hazard Assessment.

U.S. Air Force. (1989). Toluene: The Installation Restoration Toxicology Guide, Vols. 1-5. Wright-Patterson Air Force Base, OH. pp: 19.1-19-37.

U.S. EPA. (1990). Drinking water criteria document for toluene. Washington, D. C.:U. S. Environmental Protection Agency, Office of Drinking Water, ECAO-CIN-408.

U.S. EPA. (1995). Technical and Consumer Fact sheets on Toluene. National Primary Drinking Water Regulations (EPA 811-F-95-004-T).

U.S. EPA. (1985). U.S. Environmental Protection Agency. Health and Environmental Effects Profile for Methyl Methacrylate. Environmental Criteria and Assessment Office, U.S. EPA, Cincinnati, OH. ECAO-CIN-P144.

US National Library of Medicine (NLM). (2000). 2,2’azobis(isobutyronitrile). Hazardous Substances Data Bank (HSDB). Silver Platter International.

Verschueren, K. (1983). Handbook of Environmental Data on Organic Chemicals, 2nd ed. Van Nostrand Reinhold Co., New York, pp. 860-861.

Dormer W, R. Gomes and M. E. Meek. (1998). Methyl Methacrylate. Concise International Chemical Assessment Document 4. World Health Organization Geneva. ISBN: 92 4 153004 9.

Wei’an Z., Xiaofeng S., Li Y. and Yue’e F. (2003). Synthesis and characterization of poly(methyl methacrylate)/OMMT nanocomposites by y-ray irradiation polymerization. Radiation Physics and Chemistry. 67: 651-656.

W. H. B. W. Ibrahim, I. M. Mujtaba and B. M. Alhamad. (2011). Optimisation os Emulsion Copolymerization of Styrene and MMA in Batch and Semi-batch Reactors. Chemical Product and Process Modeling. Vol.6: Iss.2, Article 2.

William Bauer. (2000). Methacrylic Acid and Derivatives. Ullmann's Encyclopedia of Industrial Chemistry 2002, Wiley-VCH, Weinheim. DOI: 10.1002/14356007.a16_441.

APPENDIX A

Differentiation of Monomer Conversion

Let’s the equation of monomer conversion in the linear form:

$$x_m = \frac{1 - \frac{C_m}{C_{mo}}}{1 + \varepsilon \frac{C_m}{C_{mo}}}$$

$$x_m + \frac{\varepsilon\, C_m x_m}{C_{mo}} = 1 - \frac{C_m}{C_{mo}}$$

$$\frac{\varepsilon C_m x_m + C_m}{C_{mo}} = 1 - x_m$$

$$C_m x_m + C_m = C_{mo} - C_{mo} x_m$$

Differentiate both side of equation respected to x_m:

$$\frac{d}{dx_m}[\varepsilon C_m x_m + C_m] = \frac{d}{dx_m}[C_{mo} - C_{mo} x_m]$$

$$\varepsilon C_m + \varepsilon \mathrm{x_m} \frac{\mathrm{dC_m}}{\mathrm{dx_m}} + \frac{\mathrm{dC_m}}{\mathrm{dx_m}} = -C_{mo}$$

$$(\varepsilon x_m + 1)\frac{dC_m}{dx_m} = -C_{mo} - \varepsilon C_{mo}$$

$$\frac{dC_m}{dx_m} = -\left(\frac{C_{mo} + \varepsilon C_m}{1 + \varepsilon x_m}\right)$$

From the equation (28a),

$$\frac{dC_m}{dt} = \left(1 + \varepsilon \frac{C_m}{C_{mo}}\right) R_m$$

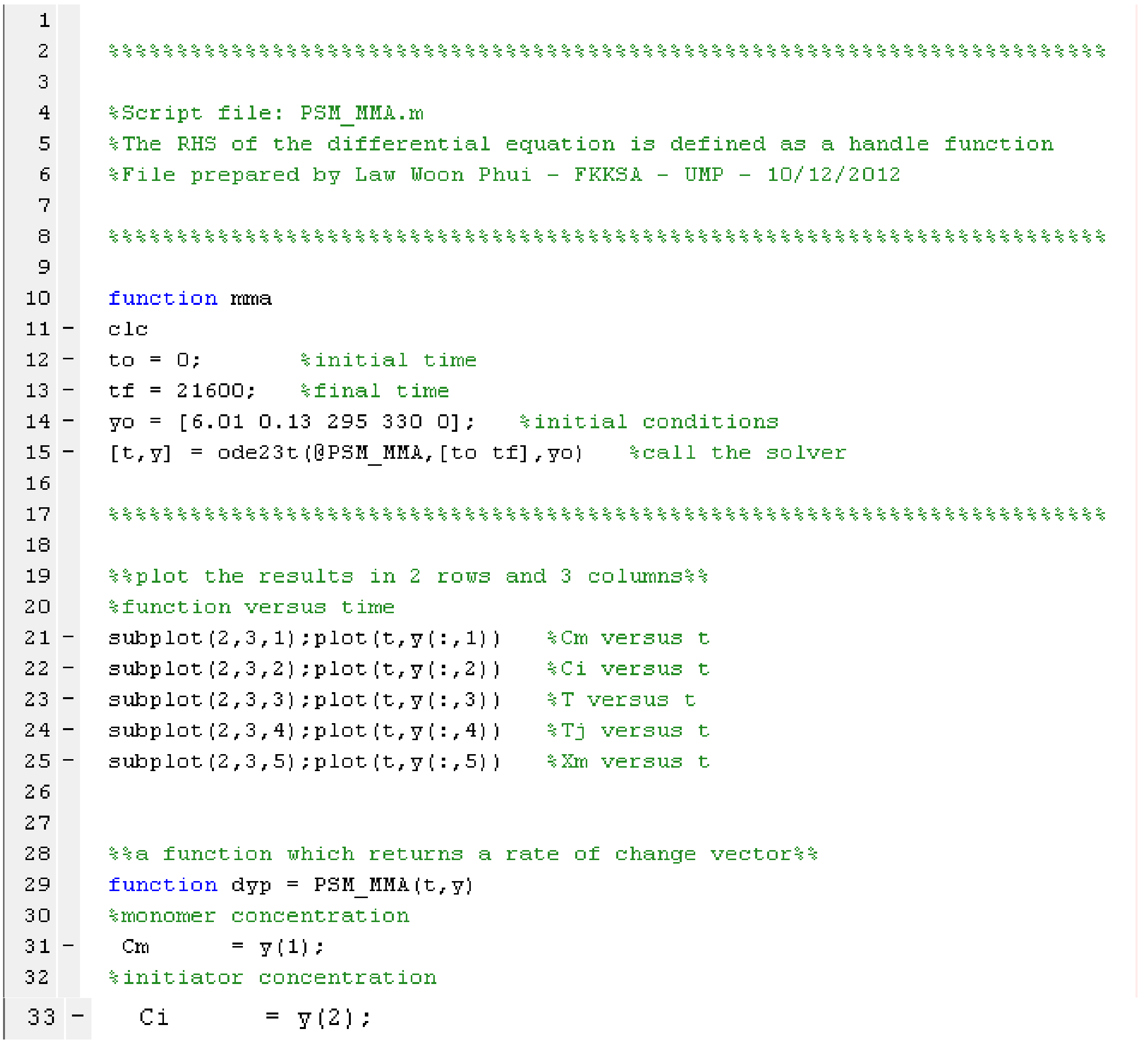
Change of monomer conversion can be calculated by using Chain Rule:

$$\frac{dx_m}{dt} = \frac{dx_m}{dC_m} \cdot \frac{dC_m}{dt}$$

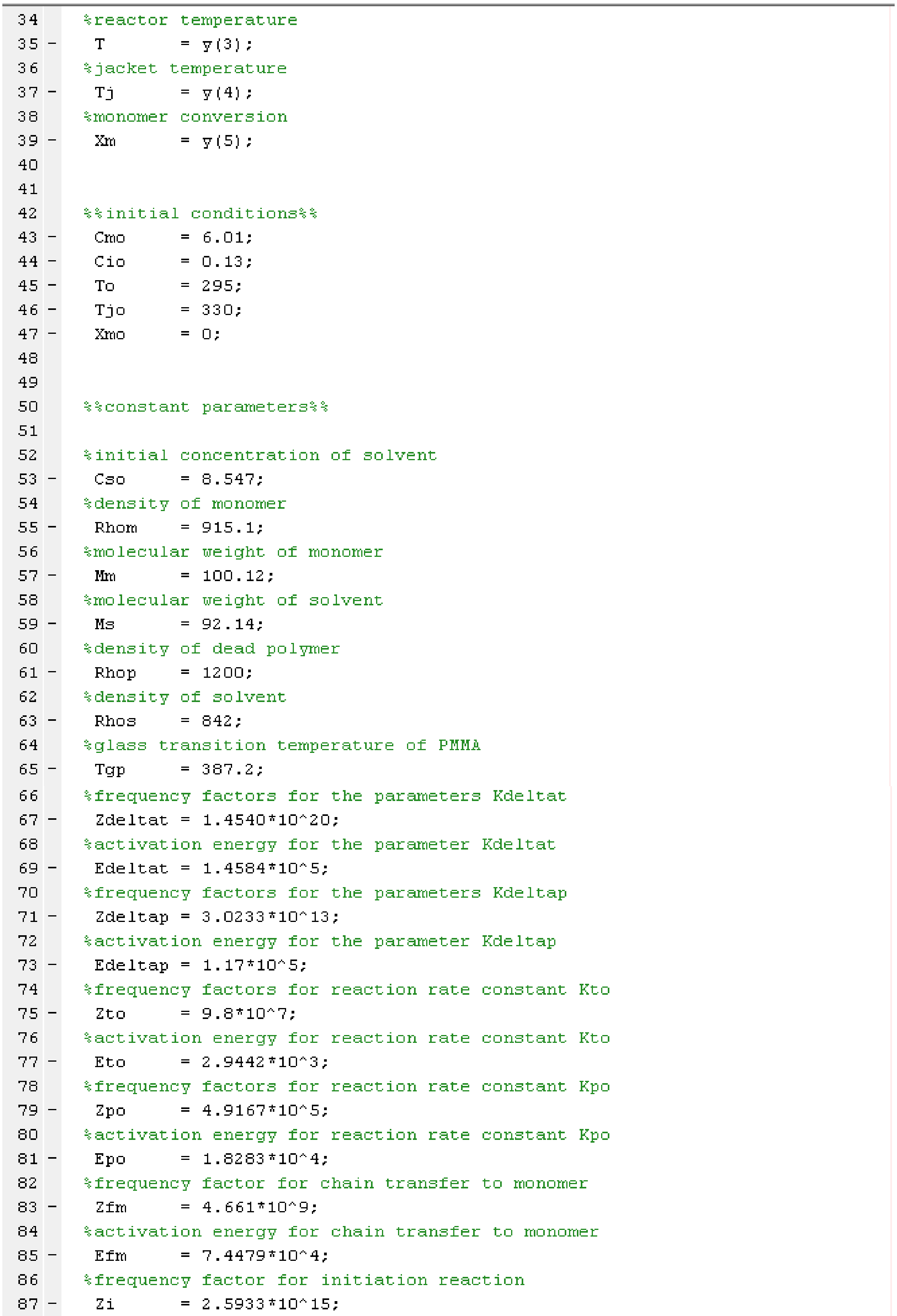
$$\frac{dx_m}{dt} = -R_m \left(\frac{1+\varepsilon x_m}{C_{m0}+\varepsilon C_m}\right)\left(1 + \varepsilon \frac{C_m}{C_{m0}}\right)$$

APPENDIX B

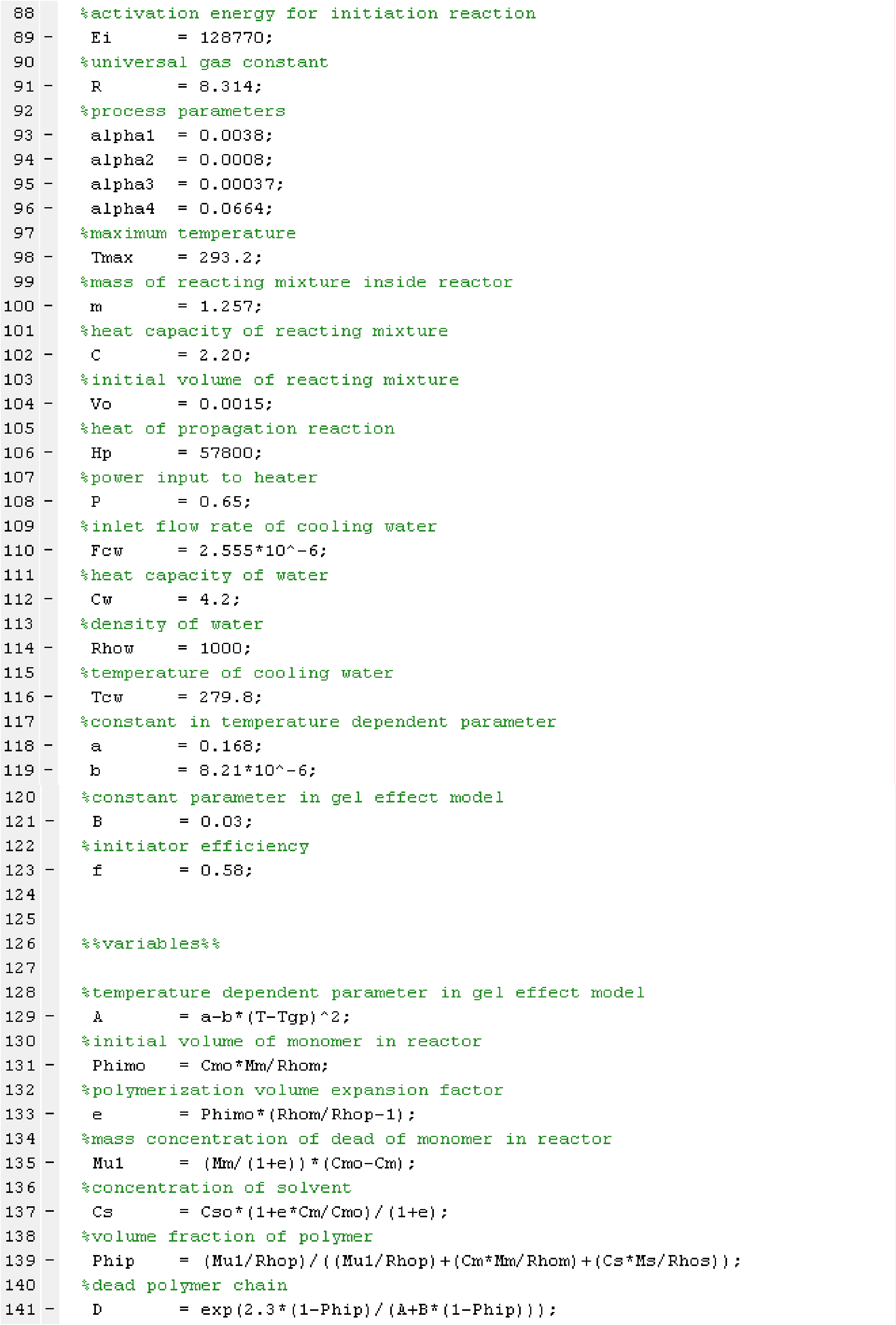
Models in MATLAB M-File



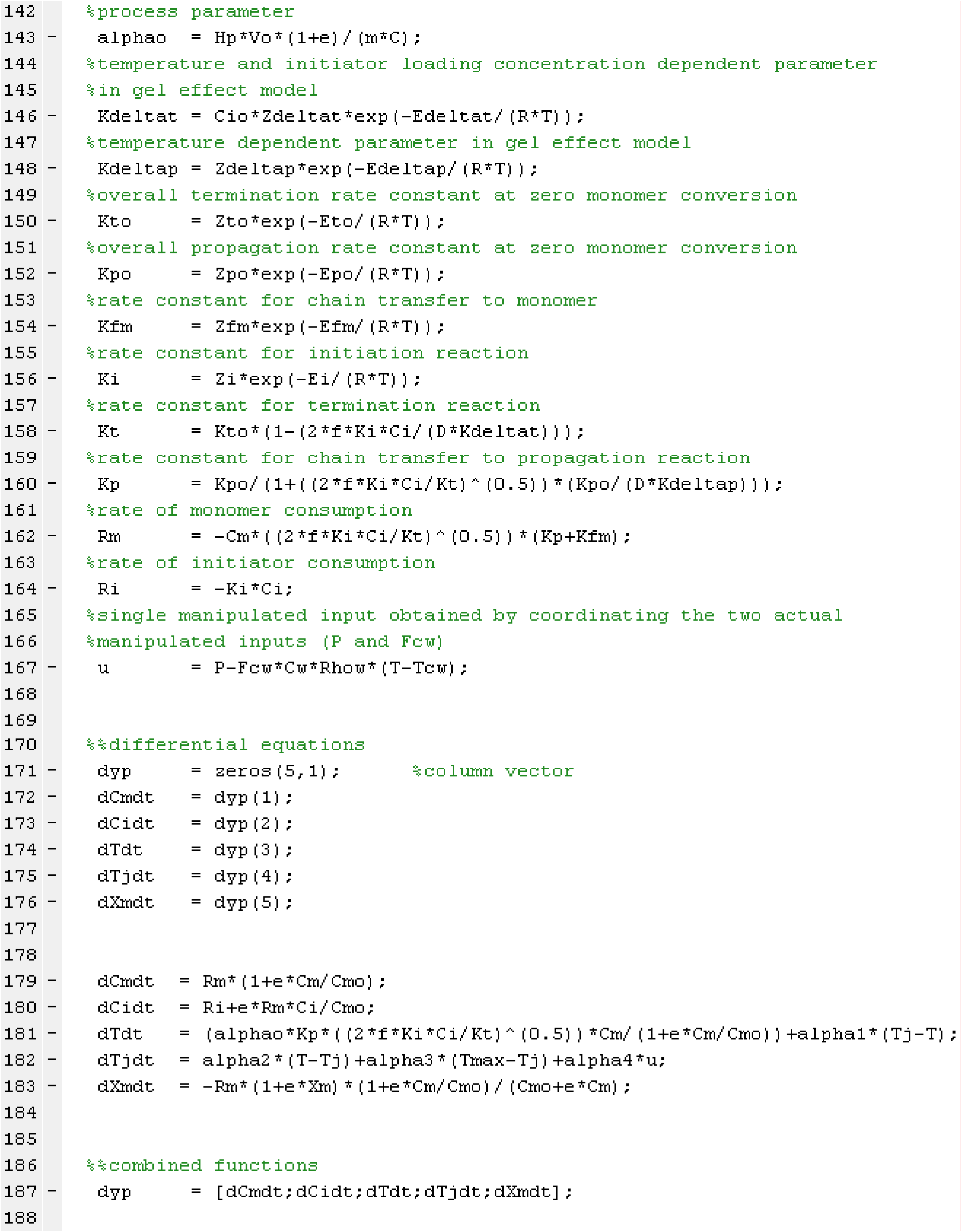
```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Script file: PSM_MMA.m
%The RHS of the differential equation is defined as a handle function
%File prepared by Law Woon Phui - FKKSA - UMP - 10/12/2012

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

function mma
clc
to = 0;        %initial time
tf = 21600;    %final time
yo = [6.01 0.13 295 330 0];   %initial conditions
[t,y] = ode23t(@PSM_MMA,[to tf],yo)   %call the solver

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%plot the results in 2 rows and 3 columns%%
%function versus time
subplot(2,3,1);plot(t,y(:,1))   %Cm versus t
subplot(2,3,2);plot(t,y(:,2))   %Ci versus t
subplot(2,3,3);plot(t,y(:,3))   %T versus t
subplot(2,3,4);plot(t,y(:,4))   %Tj versus t
subplot(2,3,5);plot(t,y(:,5))   %Xm versus t


%%a function which returns a rate of change vector%%
function dyp = PSM_MMA(t,y)
%monomer concentration
 Cm      = y(1);
%initiator concentration
 Ci      = y(2);
```



```
%reactor temperature
 T       = y(3);
%jacket temperature
 Tj      = y(4);
%monomer conversion
 Xm      = y(5);


%%initial conditions%%
 Cmo     = 6.01;
 Cio     = 0.13;
 To      = 295;
 Tjo     = 330;
 Xmo     = 0;


%%constant parameters%%

%initial concentration of solvent
 Cso     = 8.547;
%density of monomer
 Rhom    = 915.1;
%molecular weight of monomer
 Mm      = 100.12;
%molecular weight of solvent
 Ms      = 92.14;
%density of dead polymer
 Rhop    = 1200;
%density of solvent
 Rhos    = 842;
%glass transition temperature of PMMA
 Tgp     = 387.2;
%frequency factors for the parameters Kdeltat
 Zdeltat = 1.4540*10^20;
%activation energy for the parameter Kdeltat
 Edeltat = 1.4584*10^5;
%frequency factors for the parameters Kdeltap
 Zdeltap = 3.0233*10^13;
%activation energy for the parameter Kdeltap
 Edeltap = 1.17*10^5;
%frequency factors for reaction rate constant Kto
 Zto     = 9.8*10^7;
%activation energy for reaction rate constant Kto
 Eto     = 2.9442*10^3;
%frequency factors for reaction rate constant Kpo
 Zpo     = 4.9167*10^5;
%activation energy for reaction rate constant Kpo
 Epo     = 1.8283*10^4;
%frequency factor for chain transfer to monomer
 Zfm     = 4.661*10^9;
%activation energy for chain transfer to monomer
 Efm     = 7.4479*10^4;
%frequency factor for initiation reaction
 Zi      = 2.5933*10^15;
```



```
%activation energy for initiation reaction
 Ei       = 128770;
%universal gas constant
 R        = 8.314;
%process parameters
 alpha1   = 0.0038;
 alpha2   = 0.0008;
 alpha3   = 0.00037;
 alpha4   = 0.0664;
%maximum temperature
 Tmax     = 293.2;
%mass of reacting mixture inside reactor
 m        = 1.257;
%heat capacity of reacting mixture
 C        = 2.20;
%initial volume of reacting mixture
 Vo       = 0.0015;
%heat of propagation reaction
 Hp       = 57800;
%power input to heater
 P        = 0.65;
%inlet flow rate of cooling water
 Fcw      = 2.555*10^-6;
%heat capacity of water
 Cw       = 4.2;
%density of water
 Rhow     = 1000;
%temperature of cooling water
 Tcw      = 279.8;
%constant in temperature dependent parameter
 a        = 0.168;
 b        = 8.21*10^-6;
%constant parameter in gel effect model
 B        = 0.03;
%initiator efficiency
 f        = 0.58;


%%variables%%

%temperature dependent parameter in gel effect model
 A        = a-b*(T-Tgp)^2;
%initial volume of monomer in reactor
 Phimo    = Cmo*Mm/Rhom;
%polymerization volume expansion factor
 e        = Phimo*(Rhom/Rhop-1);
%mass concentration of dead of monomer in reactor
 Mu1      = (Mm/(1+e))*(Cmo-Cm);
%concentration of solvent
 Cs       = Cso*(1+e*Cm/Cmo)/(1+e);
%volume fraction of polymer
 Phip     = (Mu1/Rhop)/((Mu1/Rhop)+(Cm*Mm/Rhom)+(Cs*Ms/Rhos));
%dead polymer chain
 D        = exp(2.3*(1-Phip)/(A+B*(1-Phip)));
```



```
%process parameter
 alphao  = Hp*Vo*(1+e)/(m*C);
%temperature and initiator loading concentration dependent parameter
%in gel effect model
 Kdeltat = Cio*Zdeltat*exp(-Edeltat/(R*T));
%temperature dependent parameter in gel effect model
 Kdeltap = Zdeltap*exp(-Edeltap/(R*T));
%overall termination rate constant at zero monomer conversion
 Kto     = Zto*exp(-Eto/(R*T));
%overall propagation rate constant at zero monomer conversion
 Kpo     = Zpo*exp(-Epo/(R*T));
%rate constant for chain transfer to monomer
 Kfm     = Zfm*exp(-Efm/(R*T));
%rate constant for initiation reaction
 Ki      = Zi*exp(-Ei/(R*T));
%rate constant for termination reaction
 Kt      = Kto*(1-(2*f*Ki*Ci/(D*Kdeltat)));
%rate constant for chain transfer to propagation reaction
 Kp      = Kpo/(1+((2*f*Ki*Ci/Kt)^(0.5))*(Kpo/(D*Kdeltap)));
%rate of monomer consumption
 Rm      = -Cm*((2*f*Ki*Ci/Kt)^(0.5))*(Kp+Kfm);
%rate of initiator consumption
 Ri      = -Ki*Ci;
%single manipulated input obtained by coordinating the two actual
%manipulated inputs (P and Fcw)
 u       = P-Fcw*Cw*Rhow*(T-Tcw);


%%differential equations
 dyp     = zeros(5,1);      %column vector
 dCmdt   = dyp(1);
 dCidt   = dyp(2);
 dTdt    = dyp(3);
 dTjdt   = dyp(4);
 dXmdt   = dyp(5);


 dCmdt  = Rm*(1+e*Cm/Cmo);
 dCidt  = Ri+e*Rm*Ci/Cmo;
 dTdt   = (alphao*Kp*((2*f*Ki*Ci/Kt)^(0.5))*Cm/(1+e*Cm/Cmo))+alpha1*(Tj-T);
 dTjdt  = alpha2*(T-Tj)+alpha3*(Tmax-Tj)+alpha4*u;
 dXmdt  = -Rm*(1+e*Xm)*(1+e*Cm/Cmo)/(Cmo+e*Cm);


%%combined functions
 dyp     = [dCmdt;dCidt;dTdt;dTjdt;dXmdt];
```

Figure B.1 MATLAB M-File for PSM_MMA.m