EUGENE NG HIEN YOONG BACHELOR OF CHEMICAL ENGINEERING 2013 UMP

DYNAMIC SIMULATION OF BULK POLYMERISATION OF STYRENE USING ODE SOLVER WITHIN MATLAB SOFTWARE

EUGENE NG HIEN YOONG

UNIVERSITI MALAYSIA PAHANG

DYNAMIC SIMULATION OF BULK POLYMERISATION OF STYRENE USING ODE SOLVER WITHIN MATLAB SOFTWARE

EUGENE NG HIEN YOONG

Thesis submitted in fulfillment of the requirements for the award of the degree of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

SUPERVISOR'S DECLARATION

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

Name of Supervisor: Dr. WAN HANISAH BINTI W. IBRAHIM Position: Pensyarah Kanan Date: 23 JAN 2013

STUDENT'S DECLARATION

I declare that this report is the result of my own research except as cited in the references and summaries which have been duly acknowledge.

Signature	:
Name	: EUGENE NG HIEN YOONG
Date	: 23 JAN 2013

To my beloved family and friends

ACKNOWLEDGEMENTS

I wish to express my eternal gratitude and sincere appreciation to my supervisor, Dr. Wan Hanisah Binti W. Ibrahim, for her invaluable guidance, empowering support and profound advice throughout the preparation and realization of this thesis writing. My sincere thanks go to University Malaysia Pahang (UMP) for providing facilities and fund to support my study and librarians in UMP for providing relevant literatures.

My heartfelt gratitude also goes to my parents for their full support and cooperation to make this study possible. I cannot find the appropriate words that could properly describe my appreciation for family's devotion, supports and faith in my ability to attain my goals.

Lastly, above all, thanks to Almighty God for giving me good health, strength and perseverance to complete this proposal.

TABLE OF CONTENTS

	Page
SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
DEDICATION	iv
ACKNOWLEDGEMENT	v
LIST OF TABLES	ix
LIST OF FIGURES	Х
NOMENCLATURE	xii
ABSTRAK	xiv
ABSTRACT	xvi

CHAPTER 1 INTRODUCTION

1.1	Background of Study	1
1.2	Problem Statement	2
1.3	Research Objectives	2
1.4	Scope of Study	3
1.5	Significances of Study	3
1.6	Overview of the Study	4

CHAPTER 2 LITERATURE REVIEW

2.1	Introduction	6
2.2	Introduction to Polymer and Monomer	6
	2.2.1 Styrene and Its Properties	8
	2.2.2 Properties of Polystyrene	9
	2.2.3 Application of Polymer in Industries	10
2.3	Polymerisation Process in Batch Reactor	13

	2.3.1	Classific	ation of Polymer	13
	2.3.2	Classific	ation of Polymerisation Process	14
	2.3.3	Kinetic I	Mechanism of Free Radical Bulk	15
		Polymer	isation of Styrene	
		2.3.3.1	Initiation	15
		2.3.3	Propagation	16
		2.3.3.3	Termination	17
	2.3.4	Molecula	ar Weight Distribution	18
	2.3.5	Batch Re	eactor	19
	2.3.6	Gel and	Glass Effect	21
2.4	Dynar	nic Simula	ation Methods	22
	2.4.1	Control	Vector Parameterisation (CVP)	22
		Techniqu	ie	
	2.4.2	ODE (O	rdinary Differential Equation) Solver	24
	2.4.3	gPROM	S Software	25
	2.4.4	MATLA	B Software	26

CHAPTER 3 METHODOLOGY

3.1	Introd	uction of Methodology	28
3.2	Mathe	ematical Model Development	28
	3.2.1	Model Equations	29
	3.2.2	Parameters of the Variables	33
	3.2.3	Analysis of Degree of Freedom	34
3.3	MATI	LAB Software Computation Development	35
	3.3.1	Function M-file Creation	35
	3.3.2	Differential Equation within Function M-file	36
	3.3.3	Time Span Setting	38
	3.3.4	Initial Condition Specification	39
	3.3.5	Solver Output	39

CHAPTER 3 RESULT AND SSION

4.1	Dynamic Simulation Problem Formulation	42
4.2	Results and Discussions	44

4.2.1	Comparison Studies	47
4.2.3	Analysis of Effect of Monomer Conversion,	50
	Initiator Conversion and Initiator	
	Concentration on Batch Time	
4.2.4	Temperature Analysis Study	53

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1 0	Conclusion	57
5.2 F	Recommendation	59
REFERENC	CES	62
APPENDIC	ES	66
Appendix A	Function M-file Computation in MATLAB	66
	Software	

Appendix B Execution of ODE Solver in Command Window

68

LIST OF TABLES

Table 2.1	Styrene Monomer Physical Properties	9
Table 2.2	Properties of General Purpose Polystyrene	10
	Polymers	
Table 2.3	Type of ODE Solvers	25
Table 3.1	Parameters of Variables	33
Table 3.2	Analysis of Degree of Freedom	34
Table 4.1	Result Summary	44

LIST OF FIGURES

		Page
Figure 2.1	Styrene Monomer	7
Figure 2.2	General Form of Polystyrene (n = number	8
	repeating units)	
Figure 2.3	Polystyrene Container	12
Figure 2.4	Medical Mounting Plates with Functional Surfaces	12
Figure 2.5	First Step in Initiation Phase	16
Figure 2.6	Second Step in initiation Phase	16
Figure 2.7	Propagation Phase in Forming Polystyrene Chain	17
Figure 2.8	Termination Phase of Polystyrene Involving	18
	Combination Only	
Figure 2.9	Control Variable Approximation by Piecewise-	23
	Constant Functions	
Figure 2.10	MATLAB Software Logo	27
Figure 3.1	Function M-file Creation	36
Figure 3.2	Variables Computation within M-file	37
Figure 3.3	Parameters Computation within M-file	37
Figure 3.4	Differential Equations Computation within M-file	38
Figure 3.5	Time Span Computation in Command Window	38
Figure 3.6	Initial Value of Each Differential Equation	39
Figure 3.7	Computation of Initial Value in Command	39
	Window	
Figure 3.8	Computation of ODE15s in Command Window	40
Figure 3.9	Computation of Plot Command in Command	41
	Window	
Figure 4.1	Trend of Monomer Conversion with Batch Time	45
	in This Study	

Figure 4.2	Trend of Initial Initiator Concentration with Batch	46
	Time in This Study	
Figure 4.3	Monomer Conversion with Batch Time at Xn =	47
	500g/mol for This Study, Wan Ibrahim (2011)'s	
	Study and Ekpo (2006)'s Study	
Figure 4.4	Initial Initiator Concentration with Batch Time at	48
	$X_n = 500g/mol$ for This Study, Wan Ibrahim	
	(2011)'s Study and Ekpo (2006)'s Study	
Figure 4.5	Monomer Conversion for Run 1 ($m = 0.3$)	51
Figure 4.6	Initiator Conversion for Run 1 ($m = 0.3$)	51
Figure 4.7	Initiator Concentration for Run 1 ($m = 0.3$)	52
Figure 4.8	The Trend of Initiator Concentration with Batch	54
	Time at Different Temperature	
Figure 4.9	The Trend of Monomer Conversion with Batch	54
	Time at Different Temperature	
Figure 4.10	The Trend of Initiator Conversion with Batch	55
	Time at Different Temperature	
Figure A1	Function M-file Computation in MATLAB	66
	Software	
Figure B1	Execution of ODE Solver in Command Window	68

NOMENCLATURE

а	Density of reacting mixture
A_d	Pre-exponential Factor Initiator Decomposition, $1.58 \times 10^{15} \text{ s}^{-1}$
A_p	Pre-exponential Factor for Propagation, 1.1051 x 10 ⁷ l/gmol-s
A_t	Pre-exponential Factor for Termination, 1.255 x 10 ⁹ l/gmol-s
С	Initiator Conversion, kmol/m ³
D	Parameter in Gel Effect Equation
E_d	Activation Energy for Initiator Decomposition, 30800 cal/gmol
E_p	Activation Energy for Propagation, 7060 cal/gmol
E_t	Activation Energy for Termination, 1680 cal/gmol
f	Initiator Efficiency, 0.6
I_o	Initial Initiator Concentration, mol/l
Ι	Initiator Concentration, mol/l
<i>k</i> _d	Kinetic Constant for Initiator Decompositon, s ⁻¹
k_p	Kinetic Constant for Propagation, l/gmol-s
k_{po}	Kinetic Constant for Propagation, l/gmol-s
k_t	Kinetic Constant for Termination, l/g-mol-s
<i>k</i> _{to}	Initial Kinetic Constant for Termination, m ³ /kmol-s
<i>k</i> _n	Rate Expression for Styrene Model Equations, $n = 1, 2$
$k_{ heta p}$	Parameter in Gel Effect Equation, s ⁻¹
$k_{ heta t}$	Parameter in Gel Effect Equation, s ⁻¹

M_o	Initiator Monomer Concentration of Styrene, 8.7006 mol/l
М	Monomer Concentration of Styrene, mol/l
MW_m	Molecular Weight of Monomer, 0.10415kg/mol
т	Monomer Conversion (ξ_1)
PD	Polydispersity
R_g	Universal Gas Constant, 1.987 cal/gmol-K
X_n	Number Average Molecular Weight
X_w	Weight Average Molecular Weight
t0	Initial Batch time, 0s
t_f	Final Batch Time, s
Т	Temperature reaction, 373K
T_{gp}	Glass Transition Temperature, 373K
ξ_0	Zeroth Moment of Dead Polymer, dimensionless
ξ_1	First Moment of Dead Polymer, dimensionless
ξ2	Second Moment of Dead Polymer, dimensionless
$ ho_p$	Density of Polymer, 1060kg/m ³
μ_1	First Active Moment of Polymer, dimensionless
$ ot\!\!\!/ \!\!\!/ \!\!\!/ \! /_p$	Volume Fraction of Polymer, dimensionless

SIMULASI DINAMIK PEMPOLIMERAN PUKAL STIRENA DENGAN MENGGUNAKAN PENYELESAI ODE DALAM PERISIAN MATLAB

ABSTRAK

Tajuk kajian ini adalah untuk membangunkan simulasi dinamik pempolimeran pukal stirena dengan menggunakan penyelesai ODE dalam perisian MATLAB. Objektifobjektik kajian ini adalah untuk membangunkan penyelidikan simulasi pempolimeran pukal stirena bersama dengan pemangkin 2,2' azobisisobutyronitrile (AIBN) dalam kelompok reaktor dengan menggunakan penyelesai ODE dalam perisian MATLAB dan juga untuk menentukan jumlah awal kumpulan pemula (AIBN) yang diperlukan dan masa untuk menghasilkan nilai penukaran monomer (m) dan bilangan purata berat molekul (Xn) yang diingini pada 373K suhu tetap. Hasil kajian simulasi dalam kajian ini menggunakan perisian MATLAB dibandingkan dengan hasil yang diperolehi oleh Wan Ibrahim (2011) dengan mengunakan CVP teknik dalam perisian gPROMS dan juga hasil yang diperolehi oleh Ekpo (2006). Persamaan model dibangunkan dan diguna pakai dalam kajian ini adalah serupa dengan yang digunakan oleh Wan Ibrahim (2011) dan Ekpo (2006) dan persamaan model ini dianggap sebagai masalah nilai awal ODE dan diselesaikan dengan menggunakan penyelesai ODE15s dalam perisian MATLAB. Trend keputusan menunjukkan bahawa masa untuk penukaran monomer (m) yang lebih rendah adalah lebih rendah berbanding dengan masa untuk penukaran monomer (m)yang lebih tinggi bagi setiap bilangan purata berat molekul (Xn). Jumlah awal kumpulan pemula yang dicapai dalam kajian ini adalah lebih rendah berbanding dengan jumlah awal kumpulan pemula yang diperolehi oleh Ekpo (2006), tetapi masa yang dicapai dalam kajian ini adalah berbeza-beza berbanding dengan masa yang dicapai oleh Ekpo (2006). Berbanding dengan keputusan yang diperolehi oleh Wan Ibrahim (2011), jumlah awal kumpulan pemula yang diperlukan dalam kajian ini adalah lebih rendah daripada jumlah awal kumpulan pemula yang diperlukan dalam Wan Ibrahim (2011) kajian, tetapi masa dicapai dalam kajian ini adalah lebih panjang berbanding dengan masa yang diperolehi oleh Wan Ibrahim (2011). Kesimpulannya, penggunaan penyelesai ODE dalam perisian MATLAB dalam simulasi masalah dinamik pempolimeran pukal stirena adalah berjaya. Jumlah awal

xiv

kumpulan pemula dan masa dapat ditentukan dan keputusan yang dicapai dapat bersaing dengan keputusan yang diperolehi oleh Wan Ibrahim (2011) dan Ekpo (2006). Walau bagaimanapun, ia adalah disyorkan bahawa kajian masa depan boleh dijalankan dengan mempertimbangkan kesan rantaian pemindahan dan suhu optimum dalam kajian yang menggunakan kaedah yang sama dan perisian.

DYNAMIC SIMULATION OF BULK POLYMERISATION OF STYRENE USING ODE SOLVER WITHIN MATLAB SOFTWARE

ABSTRACT

The title of this study was to investigate the dynamic simulation of bulk polymerisation of styrene using ODE solver within MATLAB software. The objectives of this study were to develop the a simulation research on bulk polymerisation of styrene using 2,2' azobisisobutyronitrile catalyst (AIBN) catalyst in batch reactor by using ODE solver within MATLAB software and to determine the initial amount of initiator and batch time to yield desired values of monomer conversion (m) and the number average molecular weight (X_n) at fixed temperature 373K. The results later on were compared with those obtained by Wan Ibrahim (2011) using CVP technique within gPROMS software and also the results obtained by Ekpo (2006). The model equations were developed and adapted similar to those used by Wan Ibrahim (2011) and Ekpo (2006). The model equations were posed as initial value ODE problems and solved using ODE15s solver within MATLAB software. The trend of results showed that the batch time for lower monomer conversion (m) was lower compared to the batch time for higher monomer conversion (m) for each number average molecular weight (X_n) . The initial amount of initiator achieved in this study was lower compared to that obtained by Ekpo (2006) but the batch time achieved in this study varied with that obtained by Ekpo (2006). Comparing with the results obtained by Wan Ibrahim (2011), initial initiator concentration needed in this study was lower than that needed in Wan Ibrahim (2011)'s study, but the batch time achieved in this study was much higher compared to that obtained by Wan Ibrahim (2011). As a conclusion, the use of ODE solver within MATLAB software in simulating the dynamic problem of bulk polymerisation of styrene was successful. The initial amount of initiator and batch time was able to be determined and the results achieved were able to compete with the results obtained by Wan Ibrahim (2011) and Ekpo (2006). However, it was recommended that the future study could be done by considering the chain transfer effect and optimal temperature in the study using the same method and software.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Plastics are true man-made materials and these polymers have played an important role in the development of human modern civilization (Campo, 2008). Among all other polymers, polystyrene is one of the most manufactured polymers in the world from food packaging and housewares items to more durable plastic parts used in industries (Ekpo & Mujtaba, 2004; Li et al., 2011). Li et al. (2011) further stated that 8% of the world polymer market is polystyrene, featuring good stiffness, transparency and excellent processability compared to other polymers and especially rubber. Kiparissides (1996) stated that the future of polymer manufacturing industries is brighter and more exciting with the development and researches of advanced mechanistic models, molecular property estimation, model-based predictive control and optimisation of process operations in recent years. Özkan et al. (1998) and Kiparissides (2006) agreed and further emphasized that recent

developments on process modeling, optimisation and control will bring important effects towards polymer plant operability and economic.

1.2 PROBLEM STATEMENT

In today's marketplace where competition among polystyrene manufacturers are high due to the marvelous profits returned in polystyrene business. Tarafder et al. (2004) stated that a small improvement in the plant operation will significantly affect the production cost, which in turn will benefit the consumers as well. According to Gao et al. (2004), the cost of polystyrene production in batch process can be lowered by minimising the batch time meanwhile maintaining molecular weight distribution of the final polymer in a desired range. Ekpo and Mujtaba (2004) agreed and stated that optimisation in polystyrene production will definitely generate billions-Euro-ayear money. Hence, it is desirable to produce polystyrene with lower cost in industrials. In this paper, an ODE (ordinary differential equation) solver available within the MATLAB (Matrix Laboratory) software was used to simulate and investigate the initial amount of initiator towards batch time of bulk polymerisation of styrene.

1.3 RESEARCH OBJECTIVES

This study outlined the following objectives:

a) To develop a simulation research on bulk polymerisation of styrene in batch reactor by using ODE solvers within MATLAB software.

- b) To determine the initial initiator and batch time to yield specific values of monomer conversion (*m*) and the number average molecular weight (X_n) at fixed temperature.
- c) To compare the results in this study using MATLAB software with the results using gPROMS (general Process Modeling System) software in Wan Ibrahim (2011)'s study.

1.4 SCOPES OF STUDY

The scopes of this research were discussed below:

- a) Simulation researches of bulk polymerisation of styrene using 2,2' azobisisobutyronitrile catalyst (AIBN) as initiator in a batch reactor.
- b) Initial amount of initiator and its effect on monomer conversion (m), the number average of molecular weight (X_n) and batch time.
- c) Model equations in solving the simulation problem. The problem was posed as Nonlinear Programming (NLP) problem using ODE (ordinary differential equation) solvers available within the MATLAB software.

1.5 SIGNIFICANCES OF STUDY

A model which was Control Vector Parameterisation (CVP) technique had been developed and discussed in recent works. Ekpo and Mutjaba (2004) used this technique to simulate the dynamic optimisation of styrene polymerisation in batch reactors. Wan Ibrahim (2011) further improved the work from Ekpo and Mutjaba (2004) and compared the results by using gPROMS software.

Here, the significance of this study was that the researcher of this study used ODE solvers within MATLAB software to run simulation researches on the bulk polymerisation of styrene in a batch reactor using the same model equations in Wan Ibrahim (2011)'s study. If the simulation researches were successful, it signified that MATLAB software was also capable and suitable to solve any optimisation problems instead of CVP technique within gPROMS software in the future works.

Besides that, it was important to understand the effect of initial initiator on batch time in the polymerisation process while still maintaining monomer conversion and number average of molecular weight of the final polymer in a desired range. This was because the batch time would determine the polystyrene production cost and also the yield of polystyrene production in industries.

1.6 OVERVIEW OF THE STUDY

This study comprised of five main chapters including introduction in Chapter 1. Literature reviews on related researches had been discussed in Chapter 2 while Chapter 3, discussed on mathematical model development and MATLAB software computation development. Chapter 4 discussed on the dynamic simulation problem formulation and results and discussion while the last chapter reviewed on the conclusion of the study and recommendations. This study was completed with references and appendices for better understanding on the research.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter provided a literature review on the dynamic simulation of bulk polymerization of styrene using 2,2' azobisisobutyronitrile catalyst (AIBN) as initiator in a batch reactor using ODE solver within MATLAB software. Topics discussions included introduction to polymer and monomer, polymerisation process in batch reactor and lastly dynamic simulation methods. All the information could be obtained from books, articles and journals.

2.2 INTRODUCTION TO POLYMER AND MONOMER

Polymers are a group of materials that are built up of long covalently-bonded molecules, where these molecules are composed of individual units, called monomers (Nicholson, 2006; Painter & Coleman, 1997; Young & Lovell, 1991).

Polymers consist usually of multiple structural units from hundreds to more than tens of thousands, and these units are bounded together by covalent bonds (Helgesen, 2011; Odian, 2004).

The process by linking together monomer molecules is known as polymerisation and this process will be discussed further later. According to Young and Lovell (1991), the long chain which sets polymer apart from other materials will determine and give rise to the polymer characteristic properties. In this research, a type of monomer, styrene was introduced to bind chemically to form a polymer, polystyrene through polymerisation process. The figures below show general form of styrene and polystyrene.



Figure 2.1 Styrene Monomer



Figure 2.2 General Form of Polystyrene (n = number of repeating units)

2.2.1 Styrene and Its Properties

Styrene is an important monomer in the world where its products are used in an increasingly wide range of applications. According to Product Safety Bulletin (2007), 49 % of the world production of styrene monomer is consumed to produce polystyrene based on 2004 data. It is an organic compound with the chemical formula $C_6H_5CH=CH_2$ or C_8H_8 . The C_6H_5 group also makes styrene known as vinyl benzene and phenyl ethene. The presence of the vinyl group allows styrene to polymerise to form polystyrene. Figure 2.1 shows styrene monomer.

There are some properties of styrene. Firstly, it is a colorless oily liquid that evaporates easily and has a sweet smell (Nicholson, 2006). The odor threshold for styrene is 0.32 parts per million (ppm) or 4.26 mg/m³. Its molecular weight is 104.16 g/mol. The vapor pressure for styrene is 5 mm Hg at 20 °C, and its octanol/water partition coefficient (log K_{ow}) is 2.95. Styrene is slightly soluble in water, soluble in ethanol and very soluble in benzene and petroleum ether. Table below shows some of styrene monomer physical properties.

Styrene Properties				
Molecular formula	C ₈ H ₈			
Molar mass	104.15 g/mol			
Appearance	colorless oily liquid			
Density	0.909 g/cm ³			
Melting point	-30 °C, 243 K, -22 °F			
Boiling point	145 °C, 418 K, 293 °F			
Solubility in water	< 1%			
Refractive index	1.5469			
Viscosity	0.762 cP at 20 °C			

Table 2.1 Styrene Monomer Physical Properties

2.2.2 Properties of Polystyrene

Commonly, polystyrene is known as 'Styrofoam' and it is used widely in the world due to its inexpensive production cost. In chemical terms, polystyrene is a vinyl polymer, which is made from monomer styrene through polymerisation process. Structurally, it is a long hydrocarbon chain, with a phenyl group attached to every other carbon atom. Its chemical formula is $(C_8H_8)_n$. Nicholson (2006) stated that polystyrene has excellent colour range, transparency, rigidity, and low water absorption features. Odian (2004) agreed and further stated that polystyrene is a very good electrical insulator, has excellent optical clarity due to the lack of crystallinity, good resistance towards aqueous acids and bases, and is easy to fabricate into products. Figure 2.2 shows the general form of polystyrene where n is the number of monomers.

Polystyrene presents in solid or glassy state at normal temperature. When heated above its glass transition temperature, Polystyrene will deform and turn into a form that flows and can be easily used for molding and extrusion. However, it becomes solid again when temperature drops below its glass transition temperature. Table below shows some properties of general purpose polystyrene polymers.

Polystyrene Properties				
$(C_8H_8)_n$				
100°C				
1.05				
212				
390-480				
50-175				
160-200				
0.45				
6.0				
	$(C_8H_8)_n$ $100^{\circ}C$ 1.05 212 390-480 50-175 160-200 0.45 6.0			

Table 2.2 Properties of General Purpose Polystyrene Polymers (Campo, 2008)

2.2.3 Application of Polymer in Industries

According to Young and Lovell (1991), the use of polymeric materials is increasing rapidly year by year due to their capability in replacing a lot of conventional materials such as metals, wood and natural fibres such as cotton and wool. Besides that, polymer chemistry is continually advancing nowadays. In medicine, polymer is used as device to improve patient health. Examples are artificial heart and peacemakers, machines for artificial kidney dialysis and replacement joints for hips, knees and fingers (Nicholas, 2006). In food packaging industries, Nicholas (2006) further gave some examples of polystyrene such as yoghurt pots, hamburger boxes and plastic cutlery.

One of the polymeric materials, polystyrene is widely used in the word from flimsy foam packaging to more durable plastic parts used in automobiles (Ekpo and Mujtaba, 2004). According to Product Safety Bulletin (2007), polystyrene is used to produce commodity packages and consumer goods, primarily used in insulation, packaging, appliances, furniture, toys and cassettes. The main reason for the researcher of this study chose to research on bulk polymerisation of styrene in producing polystyrene was because of the increasingly significant usage of polystyrene in human daily life.

Figure 2.3 and 2.4 shows some examples of polystyrene products which are polystyrene container and medical mounting plates with functional surfaces.



Figure 2.3 Polystyrene Container



Figure 2.4 Medical Mounting Plates with Functional Surfaces

2.3 POLYMERISATION PROCESS IN BATCH REACTOR

In this topic, polymerisation process in batch reactor would be discussed and reviewed. The reviewed sub-topics covered classification of polymers, classification of polymerisation process, kinetic mechanism of free radical bulk polymerisation of styrene involving three distinct phases (initiation, propagation and termination), molecular weight distribution, batch reactor used in polymerisation process and lastly the gel and glass effect.

2.3.1 Classification of Polymers

There are several ways in classifying polymers. The most common polymer classification is introduced by Carothers in year 1929 which is based on the nature of chemical reactions employed in polymerisation. Here, the two major groups are stepgrowth polymerisation and chain polymerisation (Kiparissides, 1996; Nicholson, 2006; Painter & Coleman, 1997; Young & Lovell, 1991; Helgesen, 2011).

According to Kiparissides (1996), step-growth polymerisation (Polycondensations) usually proceeds by the reactions between two different functional groups meanwhile chain polymerisation or addition polymerisation (e.g. free radical, anionic, cationic, group transfer and coordination polymerisation) involves the full growth size of polymer chains by repeated addition of monomer molecules to an active chain center in a very short time. In chain polymerisation, a chain initiator (e.g. free radicals R^{\bullet} , anions R^{-} , cations R^{+} or coordinates compounds) is normally required for the formation of primary active centers. The difference of

these two major groups stated by Kiparissides (1996) is supported by Nicholson (2006), Painter & Coleman (1997) and Young & Lovell (1991).

The free radical chain polymerisation was applied in this study since the researcher of this study focused on the polymerisation process of monomer styrene to produce Polystyrene by using 2,2' azobisisobutyronitrile catalyst (AIBN) as initiator. No other monomer was involved in this study except monomer styrene.

2.3.2 Classification of Polymerisation Process

Generally, polymerisation process can be distinguished into bulk, solution and emulsion polymerisation. Kiparissides (1996) and Nicholson (2006) have made an overview of comparison of these three polymerisation process. In bulk polymerisation, pure monomer is used in the process with small amounts of dissolved catalyst and molecular weight modifiers. No solvent occurs in bulk polymerisation and hence the separation of the polymer product and residual monomers can be removed easily by flash evaporation or/and steam heating.

By contrast, in solution polymerisation, a monomer is dissolved in a nonreactive solvent that contains a catalyst. Although it has advantage that viscosity can be reduced compared to bulk polymerisation, however, the separation of polymer from the solution is often a costly operation.

In emulsion polymerisation, droplets of monomer are dispersed in water with the aid of an emulsifying agent. The advantages of emulsion polymerisation are low viscosity, easy thermal control and high polymerisation rate, but this polymerisation process will produce final polymer with high percentage of impurity and the production cost is higher than solution polymerisation and bulk polymerisation.

In this study, bulk polymerisation process was used because the researcher of this study focused on the software and ODE solvers that being used to solve the dynamic simulation problem of bulk polymerisation of styrene. Thus, bulk polymerisation process was chosen due to its simple and less model equations involved in simulation researches.

2.3.3 Kinetic Mechanism of Free Radical Bulk Polymerisation of Styrene

The basic mechanism for free radical bulk styrene polymerisation can be divided into three important phases, namely initiation, propagation and termination (Nicholson, 2006; Painter & Coleman, 1997; Young & Lovell, 1991; Helgesen, 2011; Wan Ibrahim, 2011).

2.3.3.1 Initiation

This phase involves creation of free-radical active centre and usually takes place in two steps. The first step is the formation of free radicals from an initiator which is 2,2' azobisisobutyronitrile catalyst (AIBN). Then, the second step is the addition of one of these free radicals to a molecule of monomer styrene. Figure 2.5 and 2.6 shows the first step and second step of initiation phase.



Figure 2.5 First Step in Initiation Phase



Figure 2.6 Second Step in Initiation Phase

In second step, an active centre is created when 2-Cyanopropyl radical generated from 2,2' azobisisobutyronitrile catalyst (AIBN) attacks the π -bond of styrene monomer. This phase ends when the active centre is formed and the next phase which is propagation starts.

2.3.3.2 Propagation

This phase involves growth of polystyrene chain by rapid sequential addition of styrene monomer to the active centre. According to Young & Lovell (1991), several thousand additions can take place within a few seconds since normally the time required for each monomer addition typically is of the order of a millisecond. Figure 2.7 shows propagation phase in forming polystyrene chain.



Figure 2.7 Propagation Phase in Forming Polystyrene Chain

2.3.3.3 Termination

In this phase, growth of polystyrene chain is terminated. The two most common mechanisms of termination are combination and disproportionation. Combination involves the coupling together of two growing chains to form a single polymer molecule. On the other side, disproportionation involves the removal of a hydrogen atom from the polymer chain to form an unsaturated final polymer. According to Hiemenz and Lodge (2007), combination and disproportional are competitive processes and do not occur to the same extent for all polymers although combination is more prevalent generally under certain circumstances. The authors further explained that the combination is more preferred at low temperature because disproportional reaction requires bond breaking which is not required for combination reaction, making more energy is required for disproportional reaction compared to that required by combination reaction. In this study, the researcher of this study followed the assumption that made by Ekpo and Mujtaba (2004) and Wan Ibrahim (2011) in developing their model equations, where the termination is by combination alone. Thus, disproportionation was neglected. The reason of following the same assumption was because the researcher of this study would like to adopt the similar model equations developed by those two studies and compare the results obtained in this study with the results obtained by those two studies. Figure 2.8 shows termination phase of polystyrene involving combination only.



Figure 2.8 Termination Phase of Polystyrene Involving Combination Only

2.3.4 Molecular Weight Distribution

According to Yoon et al. (1998), one of the most valuable polymer properties involving the physical, mechanical and rheological properties of industrial polymer is polymer molecular weight distribution. Ahmad and Tauer (2003) agreed and stated that the properties of polymer depend on size, shape and molecular weight distribution, and many applications require relatively low molecular weight polymer molecules. Yoon et al. (1998) further explained that number average molecular weight and polydispersity are used to characterise polymer molecular weight
chain length distribution polymer to have identical number average molecular weight.

Nowadays, polymerisation process conditions are always designed and operated to produce polymers of desired molecular weight properties having minimum variance values. Xie et al. (1991) determined proposed and calculated the molecular weight distribution by integrating an instantaneous chain length distribution to a desired conversion. Yoon et al. (1998) studied and determined the molecular weight distribution in styrene polymerisation initiated by a binary initiator system. The author suggested that a mixed initiator fraction is an important control variable for a new polymers which have different molecular weight distribution. Apart from that, Asteasuain et al. (2004) studied molecular weight distributions in styrene polymerisation with asymmetric bifunctional initiators. Ahmad and Tauer (2003) studied the effect of addition of chain transfer agent on the molecular weight of the polymer.

In this study, the dynamic simulation research in styrene bulk polymerisation process was studied to determine the initial amount of initiator and batch time at desired level of monomer conversion and number average molecular weight.

2.3.5 Batch Reactor

There are many simulation or optimisation researches on polymerisation process have been done using different reactors. Batch reactor or continuous stirred tank reactor (CSTR) is usually used in producing polystyrene through free radical bulk polymerisation of styrene (Costa et al., 2003; Prasad et al., 2001). However, Costa et al. (2003) studied on the numerical solution and optimisation of styrene polymerisation in tubular reactors. Hwang et al. (1998) studied thermal copolymerisation in a continuously stirred tank reactor (CSTR). Chen (2000) and Gharaghani et al. (2012) studied their works using an auto-refrigerated CSTR followed by a tubular reactor. On the other hand, Ekpo and Mutjaba (2004), Srinivasan et al. (2003), Wu et al. (1982), Frounchi et al. (2002), Wan Ibrahim (2011) and Salhi et al. (2004) used batch reactor to study different aspects in polymerisation process.

According to Ekpo & Mujtaba (2004), batch reactor has advantage over CSTR because batch reactors able to adapt the changing trends in polymer market nowadays. Ray (1986) agreed and explained that batch reactor has advantage over CSTR because it requires less auxiliary equipment and their control systems are less elaborate and costly. Özkan et al. (1998) also agreed and stated that batch or semibatch polymerisation reactors are preferred due to their production flexibility and similarity in principle to the laboratory reactor.

Besides that, Prasad et al. (2001) stated that a single CSTR operating at low conversion is not economical because of the low space-time yields. Gao et al. (2004) agreed and stated that polystyrene can only be produced at relative low temperature and conversion levels due to the limitation of mixing and heat removal capacity of CSTR. The researcher further suggested that combination of CSTR with plug flow reactor will help to solve the problems. The combination of both reactors is studied by Chen (2000) and Gharaghani et al. (2012).

The researcher of this study decided to use batch reactor in studying polymerisation process of styrene due to the simplest of the batch reactor compared to CSTR and tubular reactor. The combination of CSTR and tubular reactor is benefits, but it is costly and complicated in the process since there are two reactors involved. Moreover, this study was more focusing on the dynamic simulation of styrene polymerisation using MATLAB software.

2.3.6 Gel and Glass Effect

Gel and glass effect also known as Trommsdorff-Norrish Effect is a direct result of the localised increases in viscosity of the polymerising system that slow termination reactions. The gel and glass effect is independent of initiator concentration and is because of a decrease of the rate which polymer molecules diffuse through the viscous medium (Soots and Stanford, 1991). According to Cowie and Arrighi (2007), the significant reduction of rate of termination will directly result in the reduction of removing the radicals in the polymerisation and cause the overall radical concentration gradually increases.

A consequence of this is an increase in the number of propagation steps with the release of more heat. This will increase the rate of decomposition of initiator, thereby producing even more radicals and resulting in auto-acceleration (gel and glass effect). Runaway reactions or explosion may occur if the heat of reaction is not removed effectively (Rudin, 1999). Ekpo and Mujtaba (2004) assumed gel and glass effect is not taken into account in bulk polymerisation of styrene. Wan Ibrahim (2011) disagreed and stated that gel and glass effect is important for free radical polymerisation systems especially for bulk polymerisation where the medium is not diluted. Qin el al. (2002) also considered gel and glass effect in studying the kinetics of bulk polymerisation of styrene. In fact, in many high conversion bulk polymerisation processes, gel and glass effect always occur and affect the process (Cowie and Arrighi, 2007; Rudin, 1999). Thus, gel and glass effect was taken into account in this study since bulk polymerisation system was applied in this study. The gel and glass equations were adopted by Wan Ibrahim (2011).

2.4 DYNAMIC SIMULATION METHODS

Dynamic simulation methods must be reviewed in this study because the focus of study was on the comparison of ODE solver within MATLAB software and Control Vector Parameterisation (CVP) Technique within gPROMS software in Wan Ibrahim (2011)'s study. The reviewed sub-topics cover CVP technique, ODE solver, gPROMS software and lastly MATLAB software.

2.4.1 Control Vector Parameterisation (CVP) Technique

Control Vector Parameterisation (CVP) Technique is used to pose the dynamic optimisation problem as NLP problem which is then solved with SQP-based optimisation routines. According to Ekpo & Mujtaba (2004), this technique has the ability to handle large systems without needing to solve an excessive large optimisation problem. CVP methods are also faster than Iterative Dynamic Programming (IDP) methods (Fikar et al., 1998).

According to Paulen et al. (2010), control trajectory u(t) is first discretized to final number of intervals with constant control u_j , where $j \in \{1, \ldots, N_u\}$ indicates control interval number. Thus, an infinite-dimensional optimisation problem in continuous control variables is transformed into a finite-dimensional non-linear programming problem that can be solved by SQP-based method. Figure 2.9 shows control variable approximation by piecewise-constant functions in graph.



Figure 2.9 Control Variable Approximation by Piecewise-Constant Functions

In Wan Ibrahim (2011)'s study, this method is used to find the optimal temperature profile in a desirable monomer conversion and number average molecular weight and minimum batch time. The batch time, t is divided into finite number of intervals, Δt and a piecewise constant temperature is used is each interval, u(t). In each interval, the temperature and length of the interval are optimised.

However, CVP technique is not being applied in this study because the researcher of this study only focuses on the dynamic simulation problem. CVP technique is not suitable to simulate the dynamic simulation problem within MATLAB software for this study.

2.4.2 ODE (Ordinary Differential Equation) Solver

Mathematically, ODE (ordinary differential equation) is an equation containing a function of one independent variable and its derivatives. The derivatives are ordinary because all the derivatives involved are taken with respect to the same variable. If the equation related derivatives with respect to different variables (partial derivatives), it would be a partial differential equation.

Ordinary differential equation (ODE) is widely used in many different contexts throughout mathematics, science and engineering field because ODE can be accurately used to describe how the things changes mathematically (dynamical phenomena, evolution and variation). In polymerisation system, ODE can be used to describe the rate of decomposition, propagation and termination. The changes of amount of initiator, temperature and monomer conversion with batch time can be investigated by applying ODE.

Nowadays, ODE can be solved using advanced software like MATLAB software. The ODE solvers in the Control System toolbox of MATLAB software can accept various descriptions (Palm III, 2005). Type of ODE solvers are described in the table below.

ODE Solver	Type of Problem	Method
ODE45	Nonstiff differential equations	Runge-Kutta
ODE23	Nonstiff differential equations	Runge-Kutta
ODE113	Nonstiff differential equations	Adams
ODE15S	Stiff differential equations and DAEs	NDFs (BDFs)
ODE23S	Stiff differential equations	Rosenbrock
ODE23T	Moderately stiff differential equations and DAEs	Trapezoidal rule
ode23tb	Stiff differential equations	TR-BDF2

 Table 2.3 Type of ODE Solvers

In this study, ODE15s was chosen as the ODE solver within MATLAB because the model equations in Wan Ibrahim (2011)'s study were a set of DAE (Differential Algebraic Equations) system. ODE solver was also the simple and suitable solver to solve this set of DAE system compared to CVP technique.

2.4.3 gPROMS Software

gPROMS stands for general PROcess Modeling System. The software is the leading Advanced Process Modelling environment for the process industries. It is widely applied across many application areas in all process sectors to provide highquality information for decision support in product and process innovation, design and operation. The high-quality information for model-based decision support in process and product design and process operations can be generated using gPROMS' process modelling, process simulation and optimisation capabilities. gPROMS has many major advantages over other modelling systems on the market, resulting from its modelling power and the sophistication of the models possible. The software is however expensive costly although the price is worth for its use purpose. This was the reason for the researcher of this study decided to look for other alternative software which is less costly to study the dynamic simulation of bulk polymerisation of styrene process.

2.4.4 MATLAB SOFTWARE

MATLAB (matrix laboratory) is a numerical computing environment and fourth-generation programming language. MATLAB allows matrix manipulations, plotting of functions and data, implementation of algorithms, creation of user interfaces, and interfacing with programs written in other languages, including C, C++, Java, and Fortran. Although MATLAB is intended primarily for numerical computing, an optional toolbox uses the MuPAD symbolic engine, allowing access to symbolic computing capabilities. Besides that, an additional package, Simulink, adds graphical multi-domain simulation and Model-Based Design for dynamic and embedded systems. Figure 2.10 below shows the logo of MATLAB software.



Figure 2.10 MATLAB Software Logo

In 2004, MATLAB had around one million users throughout industrials and academics. MATLAB users come from various backgrounds of engineering, science, and economics. MATLAB is widely used in academic and research institutions as well as industrial enterprises. According to Palm III (2005), MATLAB is popular because of its long history, well developed and well tested. Other reasons are because of its user interface and compactness. The researcher of this study decided to use MATLAB software in this study because of its less costly price compared to gPROMS software. Besides that, the commands of ODE solvers within MATLAB software were easy to learn and handle.

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION OF METHODOLOGY

This chapter was the methodology of the study where mathematical model development and MATLAB software computation development were discussed and reviewed here. Other sub-topics included the model equations, the parameters of model equations, analysis of degree of freedom, function M-file creation, differential equations within function M-file, time span setting, initial condition specification and solver output.

3.2 MATHEMATICAL MODEL DEVELOPMENT

Mathematical model development included the model equations that were going to be used in the simulation researches using ODE solver within MATLAB software and also the parameters of the variables and analysis of degree of freedom.

3.2.1 Model Equations

The models equations that were going to be used in simulation researches were derived from Wan Ibrahim (2011)'s and Ekpo and Mujtaba (2004)'s studies. Both studies developed the process model used for bulk polymerisation of styrene in batch reactors, using 2,2' azobisisobutyronitrile catalyst (AIBN) as the initiator. In this present work, the gel and glass effects were considered (Wan Ibrahim, 2011).

This process model was a set of Differential-Algebraic Equations (DAEs) represented in terms of the first three moments of the dead polymer that described the molecular weight distribution changes in the batch reactor. The zeroth moment referred to the means of distribution while the first moment referred to the standard deviation and the second moment was responsible to the skewness of the distribution. The first dead moment of the dead polymer was presented as Equation (3.1). While the zeroth and second dead moments of polymer were presented as Equation (3.2) and Equation (3.3) respectively.

$$\frac{d\xi_1}{dt} = k_1 (1 - C)^{0.5} (1 - \xi_1) \tag{3.1}$$

$$\frac{d\xi_0}{dt} = ak_d(1-C) \tag{3.2}$$

$$\frac{d\xi_2}{dt} = 4k_1(1-\xi_1)(1-C)^{0.5} + 3k_2(1-\xi_1)^2 + 2ak_d I_o(1-C)$$
(3.3)

Equation (3.4) until Equation (3.6) referred to initiator conversion, initiator concentration and the relationship of initiator concentration in terms of its initial amount and conversion respectively.

$$\frac{dC}{dt} = k_d (1 - C) \tag{3.4}$$

$$\frac{dI}{dt} = -k_d I \tag{3.5}$$

$$I = I_o(1 - C) \tag{3.6}$$

Equation (3.7) until Equation (3.9) referred to number average of molecular weight (X_n) , weight average molecular weight (X_w) , polydispersity (*PD*) respectively.

$$X_w = \xi_2 / \xi_1 \tag{3.7}$$

$$X_n = \xi_1 / \xi_0 \tag{3.8}$$

$$PD = X_w / X_n \tag{3.9}$$

Density of the reaction mixture was presented as Equation (3.10).

$$a = f \frac{I_o}{M_o} \tag{3.10}$$

Equation (3.11) and Equation (3.12) were the rate expressions for the styrene model equations.

$$k_1 = k_p \left(\frac{2fk_d I_0}{k_t}\right)^{0.5} \tag{3.11}$$

$$k_2 = M_0 k_p^2 / k_t \tag{3.12}$$

Rate constant for decomposition, propagation and termination was presented from Equation (3.13) until Equation (3.15) respectively.

$$k_d = A_d exp(-\frac{E_d}{R_g T})$$
 Initiation (3.13)

$$k_{po} = A_p exp(-\frac{E_p}{R_g T}) \text{ Propagation}$$
(3.14)

$$k_{to} = A_t exp(-\frac{E_t}{R_g T})$$
 Termination (3.15)

 ξ_0 , ξ_1 , ξ_2 were the zeroth, first and second moments of the dead polymer. However, ξ_1 represented the monomer conversion and limits could be imposed on it in simulation that would reflect the fixed level of conversion which the researcher of this study want to achieve.

This model did not give a full representation of a polymerisation reaction as some assumptions had been made to reduce the complexity of the models. The assumptions were:

- a) Transfer to monomer had been neglected.
- b) Termination was by combination alone.

Since this work was considering the gel and glass effect, the extra equations were modeled in this study too. Equation (3.16) referred to the first active moment of polymer while Equation (3.17) and Equation (3.18) referred to the volume fraction of polymer and monomer concentration of styrene respectively.

$$\frac{d\mu_1}{dt} = \left[\frac{2fk_d I_o(1-C)}{k_t}\right]^{0.5} + \frac{k_p M}{k_t}$$
(3.16)

$$\phi_p = \frac{\mu_1 M W_m}{\rho_p} \tag{3.17}$$

$$M = M_o (1 - \xi_1) \tag{3.18}$$

Kinetic constant for termination and propagation was presented as Equation (3.19) and Equation (3.20).

$$k_t = \frac{k_{to}}{1 + \frac{k_{to}(\xi_0)}{D(k_{\theta t})}} \tag{3.19}$$

$$k_{p} = \frac{k_{po}}{1 + \frac{k_{po}(\xi_{0})}{D(k_{\theta}p)}}$$
(3.20)

Other parameters in gel effect equations were presented from Equation (3.21) until Equation (3.23).

$$k_{\theta p} = 2.5292 \times 10^{15} exp(-\frac{2.8 \times 10^4}{R_g T})$$
(3.21)

$$k_{\theta t} = 4.4533 \times 10^{18} I_o exp(-\frac{2.8 \times 10^4}{R_g T})$$
(3.22)

$$D = exp\left[\frac{2.303(1-\phi_p)}{0.168-8.21\times10^{-6}(T-T_{gp})^2+0.03(1-\phi_p)}\right]$$
(3.23)

The glass temperature, T_{gp} in the equations was referred to the glass transition temperature (T_g) of the polystyrene. The equation 3.17 also expressed the changing volume fraction of consumed styrene and polystyrene during the polymerisation reaction.

3.2.2 Parameters of the Variables

The parameters in model equations listed in the previous topic must be known in order to minimise the number of degree of freedom analysis. The parameters' values of almost all variables were tabulated in table 3.1.

Parameter	Value
A_d – Pre-exponential factor initiator decomposition	$1.58 \ge 10^{15} \text{ s}^{-1}$
A_p – Pre-exponential factor for propagation	1.1051 x 10 ⁷ l/gmol-s
A_t – Pre-exponential factor for termination	1.255 x 10 ⁹ l/gmol-s
E_d – Activation Energy for initiator decomposition	30800 cal/gmol
E_p – Activation Energy for propagation	7060 cal/gmol
E_t – Activation Energy for termination	1680 cal/gmol
f – Initiator efficiency	0.6
M_o – Initiator Monomer Concentration	8.7006 mol/l
R_g – Universal Gas Constant	1.987 cal/gmol-K
MW_m – Molecular Weight of Monomer	0.10415kg/mol
ρ_p – Density of Polymer	1060kg/m ³
T – Temperature of Reaction	373K
T_{gp} – Glass Transition Temperature	373K

Table 3.1 Parameters of Variables

3.2.2 Analysis of Degree of Freedom

Analysis of degree of freedom was done to determine the number of variables that were free to vary in a set of DAEs system in this study. Based on the model equations stated in previous topic, the degree of freedom was tabulated in table 3.2.

Total number of variables : $(\frac{d\xi_0}{dt}, \frac{d\xi_1}{dt}, \frac{d\xi_2}{dt}, \frac{d\mu_1}{dt}, \frac{dC}{dt}, \frac{dI}{dt}, \xi_0, \xi_1, \xi_2, C, I, k_1, k_2, k_p, k_d, k_t, k_{to}, k_{po}, I_o, k_{\theta p}, k_{\theta t}, \mu_1, \emptyset_p, t_f, D)$	25	
Total number of equations:	23	
The number of degree of freedom:	2	

 Table 3.2 Analysis of Degree of Freedom

The result of analysis of degree of freedom in the table above showed that there were only 2 variables that were free to vary in the system, which were initial amount of initiator, (I_o) and the batch time, (t_f) . This was because at the fixed temperature of reaction, the initial amount of initiator would affect the batch time. More initiator at the beginning of reaction would tend to raise the concentration of radicals formed. Thus, the batch time required to achieve the desirable molecular weight of polymer will be reduced.

3.3 MATLAB SOFTWARE COMPUTATION DEVELOPMENT

MATLAB software computation development described the methodology of using MATLAB software to compute the model equations in function M-file and run the simulation researches. The computation methodology included function M-file creation, differential equations within function M-file, time span setting, initial condition specification and solver output.

3.3.1 Function M-file Creation

The simplest way to operate MATLAB software was to enter all commands directly in the Command window. However, this simplest way was only convenient for simpler problems. When the problem needed many commands, a repeated set of commands, or had arrayed with many elements, it was inconvenient to enter all commands directly in the Command window (Palm III, 2005). Fortunately, a MATLAB program called M-file was used to write the complicate problems and run the simulations easily.

There were two types of M-file which were script file and function file. A script file also called command file contained a sequence of MATLAB commands. It was effective to avoid the need of retype commonly used procedures in Command window of MATLAB software. In contrast, function file contained all local variables, which meaning that the variables values were only available within the function. The first line in function file must begin with a function definition line that contained a list of inputs and outputs. Its syntax is as below:

function [output variables] = function_name (input variables)

In this study, a function M-file was created in MATLAB software to write the commands for the model equations listed in previous topic. The input variables were the six differential equations in the model equations which were $\frac{d\xi_0}{dt}$, $\frac{d\xi_1}{dt}$, $\frac{d\xi_2}{dt}$, $\frac{d\mu_1}{dt}$, $\frac{dC}{dt}$ and $\frac{dI}{dt}$. The output variables were ξ_0 , ξ_1 , ξ_2 , *C*, *I* and μ_1 and represented as y(1), y(2), y(3), y(4), y(5) and y(6) respectively. These output variables changed with time (*t*). The function_name was PSM_gel. The figure below showed the created function M-file.

	function ydot	=	PSM_gel(t,y)
-	zerodead	=	y(1);
-	firstdead	=	y(2);
-	seconddead	=	y(3);
-	с	=	y(4);
-	i	=	y(5);
-	muione	=	Υ (6);

Figure 3.1 Function M-file Creation

3.3.2 Differential Equations within Function M-file

Next procedure after creating a function M-file was to compute all variables, parameters of the variables and differential equations within the file. Figure 3.2 showed the computation of variable equations in the file.

	%variable	
-	kd	<pre>= Ad*exp(-Ed/(Rg*T));</pre>
-	kpo	<pre>= Ap*exp(-Ep/(Rg*T));</pre>
-	kto	<pre>= At*exp(-Et/(Rg*T));</pre>
-	rhop	= (y(6) *MWm) / Pp;
-	D	= exp((2.303*(1-rhop))/(0.168-((8.21*10^(-6))*((T-Tg)^2))+(0.03*(1-rhop)))
-	kgp	= 2.5292*10^15*exp(-2.8*10^4/(Rg*T));
-	kgt	= 4.4533*10^18*io*exp(-2.8*10^4/(Rg*T));
-	kt	<pre>= kto/(1+((kto*y(1))/(D*kgt)));</pre>
-	kp	= $kpo/(1+((kpo*y(1))/(D*kqp)));$

Figure 3.2 Variables Computation within M-file

Figure 3.3 showed the computation of parameters in the function M-file. The detailed of all aspect of parameters could be found in Table 3.1.

	%constant		
-	Т	=	374;
-	Tg	=	373;
-	MWm	=	0.10415;
-	Рр	=	1060;
-	f	=	0.6;
-	Mo	=	8.7006;
-	Ad	=	1.58*(10^15);
-	Ар	=	1.1051*(10^7);
-	At	=	1.255*(10^9);
-	Ed	=	30800;
-	Ep	=	7060;
-	Et	=	1680;
-	Rg	=	1.987;

Figure 3.3 Parameters Computation within M-file

Figure 3.4 showed the computation of six differential equations, starting from ydot(1) until ydot(4).

	%differentiate equations								
-	ydot	=	<pre>zeros(6,1);</pre>	%column vector					
-	dzerodeaddt	=	ydot(1);						
-	ddirstdeaddt	=	ydot(2);						
-	dseconddeaddt	=	ydot(3);						
-	dCdt	=	ydot(4);						
-	didt	=	ydot(5);						
-	dmuionedt	=	ydot(6);						
-	ydot(1)	=	(f*kd*y(5))/Mo;						
-	ydot(2)	=	kp*(1-y(2))*(((2	*f*kd*y(5))/kt)^0.5);					
-	ydot(3)	=	(4*kp*(1-y(2))*(((2*f*kd*y(5))/kt)^0.5))+((3*Mo*((kp*(1-y(2)))^2))/kt)+((2*f*io*y(5)*kd)/Mo);				
-	ydot(4)	=	kd*(1-y(4));						
-	ydot(5)	=	-(kd*io*(1-y(4))));					
-	ydot(6)	=	((2*f*kd*y(5)/kt)^0.5)+((kp*Mo*(1-y(2)))/kt);					
-	ydot	=	[ydot(1);ydot(2)	;ydot(3);ydot(4);ydot(5);ydot(6)];					

Figure 3.4 Differential Equations Computation within M-file

3.3.3 Time Span Setting

Time span (tspan) contained the starting and ending values of the independent variable (t) and also any intermediate values of (t) where the solution was desired. Time span could be either entered at the command window or written in M-file. Figure 3.5 showed a computation example of time span in Command window.

>>	tO	=	0;
>>	tÍ	=	8000;
>>	tspan	=	[tO, tf];

Figure 3.5 Time Span Computation in Command Window

3.3.4 Initial Condition Specification

Next procedure was to determine the initial value of the differential equations at initial time (t0 = 0). The initial value for each differential equation was shown in figure 3.6.

	%initial valu	ue
-	zerodeado	= 0.00001;
-	firstdeado	= 0.00001;
-	seconddeado	= 0.00001;
-	Co	= 0.002;
-	io	= 0.00888;
-	muioneo	= 0.00001;

Figure 3.6 Initial Value for Each Differential Equation

The parameter y0 was the value y(t0). Here, the computation of initial value for each differential equation in Command Window was shown in figure 3.7.

>> yO = [0.00001 0.00001 0.00001 0.002 0.00888 0.00001];

Figure 3.7 Computation of Initial Value in Command Window

3.3.5 Solver Output

The final procedure for the development of computation in MATLAB software was to execute the function M-file in Command Window using any solver. In this study, ODE solver was used to simulate the dynamic model equations. Generally, for the first time, ODE45 solver was used to solve the simulation problem. If ODE45 solver seemed not inefficient and the results obtained were error, then ODE15s was chosen. In this study, ODE15s solver was chosen because of the stiffness of the simulation problem and the ineffectiveness of ODE45 solver.

The basic syntax for computing the ODE solver in Command window was as below:

where function_name was the function M-file whose inputs must be t and y and whose output must be a column vector representing dy/dt or f(t,y). Thus, in this study, the computation of ODE15s in Command window was shown in figure 3.8.

>> $[t,y] = ode15s(@PSM_gel,tspan,y0)$

Figure 3.8 Computation of ODE15s in Command Window

The results obtained from the execution of ODE15s solver in Command window could be plotted using Graphics window within MATLAB software. A graphics window would automatically appear when plot command was executed. The plots generated clearly showed the trend of curve, how polymerisation system changed with time. The example of computation of plot command in Command window was as shown in figure 3.9.

Figure 3.9 Computation of Plot Command in Command Window

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 DYNAMIC SIMULATION PROBLEM FORMULATION

This chapter discussed the result on the dynamic simulation for free radical bulk polymerisation process of styrene in batch reactor. The mathematical model and MATLAB software computation development for the process were presented in chapter three. The initiator used to initiate the process was 2,2 azobisisobutyronitrile (AIBN) catalyst. The dynamic problem was solved using ODE solver within MATLAB software to find the initial initiator concentration and batch time at desired level of monomer conversion (m) and number average molecular weight (X_n) and fixed temperature. The dynamic simulation problem could be described as:

Given Fixed temperature, Fixed monomer conversion, Fixed number average molecular weight, Initial values of control variables $(\xi_0, \xi_1, \xi_2, C, I \text{ and } \mu_1)$ Simulate Values of control variables $(\xi_0, \xi_1, \xi_2, C, I \text{ and } \mu_1)$ at the end of batch time, (t_f) .

So as to determine Initial initiator concentration (I_o) and the batch time (t_f) at the fixed monomer conversion, m and number average molecular weight (X_n) .

Subject toProcess constraints: Model equations, constraints on initiatorconversion and initial initiator concentration

In this study, $m(\xi_1)$ was set at 0.3, 0.4, 0.5 and 0.6 and X_n was set at 500, 1000 or 1500. Different monomer conversions and different number average molecular weights were investigated in order to gain a clear picture of the responds of batch time and initial amount of initiator towards them. The temperature was set at 373K based on the temperature analysis on sub-topic 4.2.3 in this chapter where it was proven as one of the valid temperature for the dynamic model used in this study.

Apart from that, initial conversion, C was simulated until 1.0 (100% conversion) at the end of batch time so that there was no possible for any trace of initiator left in the reactor after the processing. It was important because the left over initiator would tend to discolour the finished polymer and lead to processing problems later on.

4.2 **RESULTS AND DISCUSSIONS**

Table 4.1 showed the result summary for the simulation problem using ODE15s within MATLAB software. The result summary also included the results obtained by Wan Ibrahim (2011) and Ekpo (2006). Figure 4.1 showed the trend of the monomer conversion (*m*) with batch time (t_f) for this study at desired level of number average molecular weight ($X_n = 500$, 1000 and 1500). While figure 4.2 showed the trend of the initial initiator concentration (I_o) with batch time (t_f) for this study at desired level of number average molecular weight ($X_n = 500$, 1000 and 1500). While figure 4.2 showed the trend of the initial initiator concentration (I_o) with batch time (t_f) for this study at desired level of monomer conversion (m = 0.3, 0.4, 0.5 and 0.6) and number average molecular weight ($X_n = 500$, 1000 and 1500).

Run	т	X_n	I _o			t_f			
			This work	Wan Ibrahim (2011)	Ekpo (2006)	This work	Wan Ibrahim (2011)	Ekpo (2006)	
1	0.3	500	0.008860	0.009143	0.008880	2360.9	2298.9	3046.3	
2	0.4	500	0.011167	0.012196	0.011167	5054.7	3338.5	5823.3	
3	0.5	500	0.014520	0.015249	0.014520	11516.0	4068.0	10816.7	
4	0.6	500	0.016559	0.018302	0.017409	21349.0	4503.2	20250.9	
5	0.3	1000	0.004125	0.004564	0.004355	10656.0	3588.4	8870.9	
6	0.4	1000	0.005400	0.006090	0.005800	19001.0	4418.3	18290.8	
7	0.5	1000	0.006595	0.007617	0.007255	29201.0	4966.0	34502.2	
8	0.6	1000	0.007800	0.009143	0.008700	42957.0	5329.3	65788.8	
9	0.3	1500	0.002622	0.003038	0.002895	18812.0	4147.7	17603.8	

Table 4.1 Result Summary

Table 4.1 Continued

Run	m	X	Io			t_f			
itun	m	π _n	This work	Wan Ibrahim (2011)	Ekpo (2006)	This work	Wan Ibrahim (2011)	Ekpo (2006)	
10	0.4	1500	0.003558	0.004055	0.003858	31700.0	4898.4	35768.8	
11	0.5	1500	0.004367	0.005073	0.004827	45761.0	5395.7	68622.8	
12	0.6	1500	0.005105	0.006090	0.005790	64120.0	5742.4	127138.0	



Figure 4.1 Trend of Monomer Conversion with Batch Time in This Study



Figure 4.2 Trend of Initial Initiator Concentration with Batch Time in This Study

The trend of the monomer conversion with batch time in the figure 4.1 above showed that the batch time for lower monomer conversion (*m*), was lower compared to the batch time for higher monomer conversion (*m*), for each number average molecular weight (X_n). For $X_n = 500$ g/mol, t_f was 2360.9s, 5054.7s, 11516.0s and 21349.0s for m = 0.3, 0.4, 0.5 and 0.6. From figure 4.2, the initial amount of initiator needed for each monomer conversion was decreasing with the increasing of number average molecular weight. For m = 0.3, I_o needed was 0.008860mol/1, 0.004125mol/1 and 0.002622mol/1 for Xn = 500g/mol, 1000g/mol and 1500g/mol respectively. According to Wan Ibrahim (2011), lower initial amount of initiator would produce less primary free radical at the beginning of the process and this would contribute to the increase of chain length in propagation process. Thus, number average of molecular weight tended to increase. However, the increase of molecular weight would lead to the longer batch time required in the process as shown in the figure 4.1 and figure 4.2.

4.2.1 Comparison Studies

Comparison studies were done to compare the results obtained by applying ODE solver within MATLAB software in this study with the results obtained by applying CVP technique within gPROMS software in Wan Ibrahim (2011)'s study. Moreover the results obtained by Ekpo (2006) were also compared. Figure 4.3 showed the monomer conversion with batch time at $X_n = 500$ g/mol for this study, Wan Ibrahim (2011)'s study and Ekpo (2006)'s study. Figure 4.4 showed the initial initiator concentration with batch time at $X_n = 500$ g/mol for this study, Wan Ibrahim (2011)'s study and Ekpo (2006)'s study.



Figure 4.3 Monomer Conversion with Batch Time at $X_n = 500$ g/mol for This Study, Wan Ibrahim (2011)'s Study and Ekpo (2006)'s Study



Figure 4.4 Initial Initiator Concentration with Batch Time at $X_n = 500$ g/mol for This Study, Wan Ibrahim (2011)'s Study and Ekpo (2006)'s Study.

Comparing the results in Ekpo (2006)'s study, the result obtained in this study was much better in terms of initial amount of initiator and batch time. For each monomer conversion, the initial amount of initiator needed in this study was lower compared to the initial initiator in Ekpo (2006)'s study. For m = 0.3, 0.4, 0.5 and 0.6 at $X_n = 500$ g/mol, I_o needed in this study was 0.008860mol/l, 0.011167mol/l, 0.014520mol/l and 0.016559mol/l, while I_o needed in Ekpo (2006)'s study was 0.008880mol/l, 0.011167mol/l, 0.014520mol/l and 0.017409mol/l. For $X_n = 1000$ g/mol and $X_n = 1500$ g/mol, I_o needed in this study also was lesser than I_o needed by Ekpo (2006).

The batch time for each monomer conversion in this study varied compared to the batch time in Ekpo (2006)'s study. For m = 0.3, 0.4, 0.5 and 0.6 at $X_n =$ 500g/mol, t_f obtained in this study was 2360.9s, 5054.7s, 11516.0s and 21349.0s, while t_f obtained in Ekpo (2006)'s study was 3046.3s, 5823.3s, 10816.7s and 20250.9s. For $X_n = 1000$ g/mol and $X_n = 1500$ g/mol, t_f obtained in this study also varied with t_f obtained by Ekpo (2006). This was because Ekpo (2006)'s study did not consider gel and glass effect but the researcher of this study did consider it. Ekpo (2006)'s study made assumption that gel and glass effect was being neglected and it was free volume. However, through this study, it was proven that gel and glass effect and also volume fraction were important that would affect the results and could not be neglected.

Besides that, the result obtained in this study was compared with Wan Ibrahim (2011)'s study. The comparison showed that the initial amount of initiator needed in this study was lower than the initial amount of initiator needed in Wan Ibrahim (2011)'s study for each monomer conversion and number average of molecular weight. For m = 0.3, 0.4, 0.5 and 0.6 at $X_n = 500$ g/mol, I_o needed in this study was 0.008860mol/l, 0.011167mol/l, 0.014520mol/l and 0.016559mol/l, while I_o needed in Wan Ibrahim (2011)'s study was 0.009143mol/l, 0.012196mol/l, 0.015249mol/l and 0.018302mol/l. For $X_n = 1000$ g/mol and $X_n = 1500$ g/mol, I_o needed in this study also was lesser than I_o needed by Wan Ibrahim (2011).

However, the batch time required in Wan Ibrahim (2011)'s study was much lower compared to the batch time simulated in this study using ODE solver. For m =0.3, 0.4, 0.5 and 0.6 at $X_n = 500$ g/mol, t_f obtained in this study was 2360.9s, 5054.7s, 11516.0s and 21349.0s, while t_f obtained in Wan Ibrahim (2011)'s study was 2298.9s, 3338.5s, 4068.0s and 4503.2s. For $X_n = 1000$ g/mol and $X_n = 1500$ g/mol, t_f obtained in this study was also higher with t_f obtained by Wan Ibrahim (2011). This was because this study focused in the simulation researches problem using ODE solver within MATLAB software at the fixed temperature (single interval temperature) while Wan Ibrahim (2011)'s study focused on the optimisation of optimal temperature (three interval temperature) and initial initiator concentration using CVP technique within gPROMS software. According to Gao et al. (2004), the right combination of temperature and amount of initiator would reduce bath time significantly. Thus, it was concluded that Wan Ibrahim (2011)'s results were better than this study's results.

4.2.2 Analysis of Effect of Monomer Conversion, Initiator Conversion and Initiator Concentration on Batch Time

It was important to understand the effect of monomer conversion, initiator conversion and initial initiator concentration on batch time in the polymerisation process while still maintaining monomer conversion and number average of molecular weight of the final polymer in a desired range. This was because the batch time would determine the polystyrene production cost and the yield of polystyrene production in industries. In this sub-topic, the analysis of effect of monomer conversion, initiator conversion and initial initiator concentration on batch time were done for Run 1 (m = 0.3).

Figure 4.5 showed the monomer conversion for Run 1 (m = 0.3) while Figure 4.6 showed the initiator conversion for Run 1 (m = 0.3). Figure 4.7 showed the initiator concentration for Run1 (m = 0.3).



Figure 4.5 Monomer Conversion for Run 1 (m = 0.3)



Figure 4.6 Initiator Conversion for Run 1 (m = 0.3)



Figure 4.7 Initiator Concentration for Run 1 (m = 0.3)

The trend of curve in Figure 4.5 showed that monomer conversion was increasing with the batch time. This meant that initiators appeared in the polymerisation process where primary radical was formed at the beginning of the process. The radical would initiate the polymerisation process and monomers would start to polymerise and forming a polymer chain. The longer batch time would cause more and more monomers to polymerise during the propagation process.

While the decomposition of initiator was increasing with the batch time, the initiator conversion would start increasing as shown in Figure 4.6. The initiator conversion would reach almost 1.0 when the decomposition of initiator was at its maximum. The maximum decomposition of initiator referred to the depletion of initiator in the polymerisation process. Thus, the initiator concentration was decreasing with batch time as shown in Figure 4.7.

The depletion of initiator did not mean that the polymerisation process ended. The chain length of the Polystyrene during propagation process would continue until the desire number average of molecular weight was obtained. Then, the termination process would occur and terminate the bulk polymerisation process.

4.2.3 Temperature Analysis Study

In this sub-topic, different temperature was analysed to determine the effect of temperature towards the initiator concentration, monomer conversion, initiator conversion and batch time. The temperature used was 350K, 360K, 370K and 373K. In order to study the effect of temperature, the initial initiator concentration, I_0 was set at 0.00886mol/1. The dynamic model equations in Chapter 3 were used and solved as initial value problems in ODE solver within MATLAB software. Figure 4.8 showed the trend of initiator concentration with batch time at different temperature. Figure 4.9 showed the trend of monomer conversion with batch time at different temperature. Figure 4.10 showed the trend of initiator conversion with batch time at different temperature.



Figure 4.8 The Trend of Initiator Concentration with Batch Time at Different Temperature



Figure 4.9 The Trend of Monomer Conversion with Batch Time at Different Temperature


Figure 4.10 The Trend of Initiator Conversion with Batch Time at Different Temperature

From figure 4.8, at 373K, the decrease of initiator concentration was the fastest, followed by the decrease of initiator concentration at 370K, 360K and lastly 350K. This was because the bonding of AIBN initiator was easily to break and decompose at high temperature compared to that at low temperature. As more initiators decomposed and formed initiator radicals, the initiator conversion tended to increase. Thus, the initiator conversion was the fastest at 373K as shown in figure 4.10, followed by at 370K, 360K and lastly 350K.

From figure 4.9, monomer conversion at 373K was the highest at the beginning process and followed by the monomer conversion at 370K, 360K and 350K. This was due to the high decomposition of initiators at the beginning process under high temperature, causing more monomers were added to the initiator radicals and forming the polymer chains. However, the initiator concentration was limited, meaning that the decomposition of initiators would end when there was no initiator

left in the reactor. Thus, the monomer conversion would start to slow down. Slowly with the batch time, the monomer conversion at low temperature would higher than the monomer conversion at high temperature. The monomer conversion would continue increasing with time due to the propagation process. When reaching the desired level of molecular weight, the polymer chain would be terminated and polystyrene was formed.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Dynamic simulation of bulk polymerisation of styrene using ODE solver within MATLAB software was examined. The mathematical model equations that required in this study was determined, developed and adopted from Wan Ibrahim (2011)'s study. The model equations were posed as ODE initial value problems and successfully executed using ODE15s within MATLAB software.

The initial amounts of initiator concentration that needed in the process and the batch time at the desired level of monomer conversion and number average molecular weight were determined from the ODE simulation result. The trend of the result in the table 4.1 showed that the initial amount of initiator needed for each monomer conversion was decreasing with the increasing of number average molecular weight, similar to the trend of results achieved by Wan Ibrahim (2011) using CVP technique within gPROMS software. This proved that MATLAB software could be used to simulate the similar works done using gPROMS software and its advantages were less costly and easily handling compared to gPROMS software.

From the result, the initial amount of initiator needed and batch time for this study was lower compared to that obtained by Ekpo (2006) using CVP technique. This was because this study had considered gel and glass effect in the development of gel and glass effect, adopted from the model equations purposed by Wan Ibrahim (2011) using CVP technique within gPROMS software. The initial initiator concentration needed was lower compared to that achieved by Wan Ibrahim (2011). However, the batch time at the desired level of monomer conversion and number average molecular weight for this study was much higher than the batch time obtained by Wan Ibrahim (2011). This was because this study only focused on the dynamic simulation problem using ODE solver within MATLAB software instead of dynamic optimisation work done by Wan Ibrahim (2011) using CVP technique within gPROMS software. The comparison results would lead to recommendation of the future work for this study.

The effect of monomer conversion, initiator conversion and initiator concentration on batch time were investigated. Monomer conversion was increasing with the batch time, meaning that initial process was beginning. While the decomposition of initiator was increasing with the batch time, the initiator conversion would start increasing as shown in Figure 4.6, reflecting that the initiator concentration was decreasing with batch time as shown in Figure 4.7.

The temperature analysis study was also done. It was concluded that temperature had effect towards the rate of polymerisation process. At high temperature, initiator would decompose faster, causing its concentration decreased faster than the decrease of initiator concentration at low temperature. Temperature also showed effect towards monomer conversion in this study. In the beginning process, monomer conversion at high temperature was higher than the monomer conversion at low temperature. However, for a long time period of process, the monomer conversion at low temperature was higher than the monomer conversion at high temperature. This temperature analysis results would lead to recommendation of the future work for this study because this study fixed the temperature at 373K.

As a conclusion, this study's objectives were successfully achieved where MATLAB software was capable and able to simulate the dynamic problems in the polymerisation processing system applying the same model equations in Wan Ibrahim (2011)'s study using CVP technique within gPROMS software. The initial amount of initiator and batch time at desired level of monomer conversion and number average molecular weight was able to be determined and compared with those obtained by Ekpo (2006) and Wan Ibrahim (2011).

5.2 **RECOMMENDATIONS**

This study focused on the dynamic simulation of bulk polymerisation of styrene in batch reactor using AIBN catalyst. The dynamic problem was posed as initial value problem and is solved using ODE15s solver within MATLAB software successfully. This proved that MATLAB was able to solve the similar model equations developed by Wan Ibrahim (2011) using CVP technique within gPROMS software. It is recommended that the future work can be done using the same method to investigate the dynamic optimisation of bulk polymerisation of styrene instead of investigate the dynamic simulation of bulk polymerisation of styrene. It is clearer to see the difference of results under same model equations and topic, but different technique and software.

In this study, few assumptions had been made to reduce the complexity of the models according to Ekpo and Mutjaba (2004). The assumptions were:

- a) Transfer to monomer has been neglected.
- b) Termination is by combination alone.

It is recommended to consider chain transfer to monomer in the bulk polymerisation process of styrene. According to Ahmand and Tauer (2003), molecular weight of the polymer can be reduced by adding a small amount of chain transfer agent, which brings about the termination of the growing polymer and initiation of a new chain. Ahmad and Tuer (2003)' study showed that the number average molecular weight decreases with the increase of chain transfer agent and, on average, the mobility of polymer chains increases and this automatically leads to higher termination rate.

In this study, the temperature was fixed at 373K in this study to do the simulation researches. However, based on the temperature analysis done in sub-topic

4.2.3, the selection of temperature was important as it would affect the rate of decomposition of initiators. Thus, it is recommended that optimal temperature should be applied in the study so as to determine the initial amount of initiator and minimum batch time, similar to the work done by Wan Ibrahim (2011). According to Gao et al. (2004), the right combination of temperature and amount of initiator would reduce bath time significantly.

REFERENCES

- Ahmad, H., & Tauer, K. (2003). Effect of Chain Transfer Agent on the Radical Polymerization of Styrene in Non-aqueous Dispersion, *Colloid Poly Sci*, 281, 686-689.
- Asteasuain, M., Brandolin, A., & Sarmoria, C. (2004). Molecular Weight Distribution in Styrene Polymerization with Asymmetric Bifunctional Initiators, *Polymer*, 45, 321-335.
- Campo, E. A. (2008). *Industrial Polymers*. Germany: Hanser Gardner Publications, Inc.
- Chen, C.C., (2000). Continuous Production of Solid Polystyrene in Back-mixed and Linear-flow Reactors, *Polym. Eng. Sci.*, 40, 441-464.
- Chmúrny, D., Prokop, R., & Bakošová, M. (1988), *Automatic Control of Technological Processes*. Alfa. Bratislava. (in Slovak).
- Costa, E. F., Lage, P. L. C., & Biscaia, E. C. (2003). On the Numerical Solution and Optimization of Styrene Polymerization in Tubular Reactors., *Comput. Chem. Eng.*, 27, 1591-1604.
- Cowie, J. M. G., & Arrighi, V. (2008). *Polymers: Chemistry and Physics of Modern Materials* (3rd Ed.). Florida, U.S.: CRC Press Taylor & Francis Group, LLC.
- Dub é, M.A., Soares, J. B. P., Penlidis, A., & Hamielec, A. E. (1997). Mathematical Modeling of Multicomponent Chain-Growth Polymerizations in Batch, Semibatch, and Continuous Reactors: A Review, *Ind. Eng. Chem. Res.*, 36, 966-1015.
- Ekpo, E. E. (2006). Dynamic Optimisation and Control of Batch Polymerisation Process, Ph.D. thesis, University of Bradford.
- Ekpo, E. E., & Mujtaba. I. M. (2004). Dynamic Optimisation of Styrene Polymerisation in Batch Reactors, *European Symposium on Computer-Aided Process Engineering - 14, Book Series: Computer-Aided Chemical Engineering*, Vol. 18, 649-654, 2004, Lisbon, Portugal.

- Fikar, M., Latifi, M. A., Fournier, F., & Creff, Y. (1998). CVP versus IDP in Dynamic Optimisation of a Distillation Column, *Computers chem. Engng.*, 22, S625-S628, 1998.
- Frounchi, M., Farhadi, F., & Mohammadi, R. P. (2002). Simulation of Styrene Radical Polymerisation in Batch Reactor: A Modified Kinetic Model for High Conversion, *Scientica Iranica*, 9(1), 86-92.
- Gharaghani, M., Abedini, H., & Parvazinia, M. (2012). Dyanamic Simulation and Control of Auto-refrigerated CSTR and Tubular Reactor for Bulk Styrene Polymerisation, *Chem. Eng. Res. Des.*, 90, 1540–1552.
- Gao, J., Hungenberg, K. D., & Penlidis, A. (2004). Process Modeling and Optimization of Styrene Polymerization, *Macromol. Symp.*, 206, 509-522.
- Helgesen, A. H. (2011). Toolbox for Generation of Nonlinear Control Models for Semi Batch Emulsion Polymerization Reactors, Master's thesis, Norwegian University of Science and Technology.
- Hiemenz, P. C., & Lodge, T. P. (2007). *Polymer Chemistry* (2nd Ed.). Florida, U.S.: CRC Press Taylor & Francis Group, LLC.
- Hwang, W. H., Chey, J. I., & Rhee, H. K. (1998), Modeling and Control of Continuous Stirred Tank Reactor for Thermal Copolymerization, *Journal of Applied Polymer Science*, 67(5), 921-931.
- Kiparissides, C. (1996). Polymerization Reactor Modeling: A Review of Recent Developments and Future Directions, *Chem. Eng. Sci.*, 51(10), 1637-1659.
- Kiparissides, C. (2006). Challenges in Particulate Polymerization Reactor Modeling and Optimization: A Population Balance Perspective, *Journal of Process Control*, 16, 205-224.
- Li, L., Gomes, C. S. B., Lopes, P. S., Gomes, P. T., Diogo, H. P., & Ascenso, J. R. (2011). Polymerization of Styrene with Tetradentate Chelated α-diimine Nickel(II) Complexes/MAO Catalyst Systems: Catalytic Behavior and Microstructure of Polystyrene, *European Polymer Journal*, 47, 1636-1645.
- Mikleš, J., & Fikar, M. (2007). *Process Modelling, Identification, and Control.* Berlin: Springer Verlag.
- Nicholson, J. W. (2006). *The Chemistry of Polymers*. Cambridge, UK: The Royal Society of Chemistry.
- Odian, G. (2004). *Principles of Polymerization* (4th Ed.). New Jersey, U.S.: John Wiley & Sons, Inc.

- Özkan, G., Hapoglu, H., & Alpbaz, M. (1998). Generalized Predictive Control of Optimal Temperature Profiles in a Polystyrene Polymerization Reactor, Chemical Engineering and Processing, 37, 125-139.
- Painter, P. C., & Coleman, M. M. (1997). Fundamentals of Polymer Science. Florida, U.S.: CRC Press.
- Palm III, W. J. (2005). *Introduction to MATLAB 7 for Engineers*. U.S.: McGraw-Hill Companies, Inc.
- Paulen, R., Fikar, M., & Latifi, M. A. (2010). "Dynamic Optimization of a Polymerization Reactor," Control & Automation (MED), 2010 18th Mediterranean Conference on , 733-738.
- Prasad, V., Schley, M., Russo, L. P., & Bequette, B. W. (2001). Product Property and Production Rate Control of Styrene Polymerisation, *Journal of Process Control*, 12, 353-372.
- Product Safety Bulletin. (2007). *Styrene Monomer*. Texas, North America: Lyondell Chemical Company.
- Qin, J., Guo, W., & Zhang, Z. (2002). A Kinetic Study of Bulk Polymerisation of Styrene, *Polymer*, 43, 7521-7527.
- Raja, T. M. (1995). Modelling and control of the Polymerisation of Styrene, Ph.D. thesis, University of Bradford.
- Rudin, A. (1999). The Elements of Polymer Science and Engineering (2nd Ed.). San Diego, U.S.: Academic Press.
- Salhi, D., Daroux, M., Gentric, C., Corriou, J. P., Pla, F., & Latifi, M. A. (2004). Optimal Temperature – Time Programming in a Batch Copolymerization Reactor, *Ind. Eng. Chem. Res.*, 43, 7392-7400.
- Srinivasan, B., Palanki, S., Bonvin, D. (2003). Dynamic Optimization of Batch Processes I. Characterization of the Nominal Solution, *Computers Chem. Eng.*, 27, 1-26.
- Soots, C., & Stanford, T. (1991). "Modeling the polymerization process-the geleffect function," System Theory, 1991. Proceedings., *Twenty-Third Southeastern Symposium on*, 428-434.
- Tarafder, A., Rangaiah, G. P., & Ray, A. K. (2004). Multiobjective Optimization of an Industrial Styrene Monomer Manufacturing Process, *Chem. Eng. Sci.*, 60, 347-363.

- Wan Ibrahim, W. H. B. (2011). Dyanmic Modelling and Optimization of Polymerization Processes in Batch and Semi-Batch Reactors, Ph.D. thesis, University of Bradford.
- Wu, G. Z. A., Denton, L. A., & Laurence, R. L. (1982). Batch Polymerization of Styrene-optimal Temperature Histories, *Polymer Engineering and Science*, 22 (1), 1–8.
- Xie, T., Hamielec, A. A., Wood, P. E., & Woods, D. R. (1991). Experiment Investigation of Vinyl Chloride Polymerization at High Conversion: Molecular-Weight Development, *Polymer*, 32(6), 1098.
- Yoong, W. J., Ryu, J. H., & Park, Y. H. (1998). Calculation of Molecular Weight Distribution in Styrene Polymerization Initiated by a Binary Initiator System, *Korean J. Chem. Eng.*, 15(3), 330-335.
- Young, R. J., & Lovell, P. A. (1991). *Introduction To Polymers* (2nd Ed.). Florida, U.S.: CRC Press.

APPENDICES

APPENDIX A – Function M-file Computation in MATLAB Software

Editor - C:\MATLAB7\work\PSM_gel.m								
File	Ed	lit Text Cell Tool	ls Debug Desktop Window Help					
n	<u>a</u>		🗠 🖓 🎒 🕈 🔒 👷 🗐 🍘 🛍 🗈 🕼 Stack Base 🔽					
2		5 ↓8 ↓8 - 1.0	+ + + 1.1 × %°+ %°+					
1		function ydot	= PSM_gel(t,y)					
2	-	zerodead	= y(1);					
3	-	firstdead	= y(2);					
4	-	seconddead	= y(3);					
5	-	с	= y(4);					
6	-	i	= y(5);					
7	-	muione	= \bar{y}(6);					
8								
9		%initial value	e					
10	-	zerodeado	= 0.00001;					
11	-	firstdeado						
12	-	seconddeado						
13	-	Co	= 0.002;					
14	-	10						
15	-	muloneo	= 0.00001;					
10								
10	_	⊰constant T	- 274.					
10	_	I Ter	- 374;					
20	_	IG MUm	- 575;					
20	_	nwin Pr	= 10:00:					
22	_	f	= 0.6.					
23	_	± Mo						
24	_	bd	$= 1.58 * (10^{15})$					
2.5	_	An	$= 1.1051 \times (10^{-7})$:					
26	_	At	$= 1.255*(10^9):$					
27	_	Ed	= 30800;					
28	-	Ep	= 7060;					
29	-	- Et	= 1680;					
30	-	Rg	= 1.987;					

Figure A1 Function M-file Computation in MATLAB Software

31						
32	%variable					
33 -	kd	<pre>= Ad*exp(-Ed/(Rg*T));</pre>				
34 -	kpo	<pre>= Ap*exp(-Ep/(Rg*T));</pre>				
35 -	kto	<pre>= At*exp(-Et/(Rg*T));</pre>				
36 -	rhop	= (y(6) *MWm)/Pp;				
37 -	D	= exp((2.303*(1-rhop))/(0.168-((8.21*10^(-6))*((T-Tg)^2))+(0.03*(1-rhop))));				
38 -	kgp	= 2.5292*10^15*exp(-2.8*10^4/(Rg*T));				
39 -	kgt	= 4.4533*10^18*io*exp(-2.8*10^4/(Rg*T));				
40 -	kt	<pre>= kto/(1+((kto*y(1))/(D*kgt)));</pre>				
41 -	kp	= kpo/(1+((kpo*y(1))/(D*kgp)));				
42						
43	%differentiate equations					
44 -	ydot	= zeros(6,1); %column vector				
45 -	dzerodeaddt	= ydot(1);				
46 -	ddirstdeaddt	= ydot(2);				
47 -	dseconddeaddt	; = ydot(3);				
48 -	dCdt	= ydot(4);				
49 -	didt	= ydot(5);				
50 -	dmuionedt	= ydot(6);				
51						
52						
53 -	ydot(1)	= (f*kd*y(5))/Mo;				
54 -	ydot(2)	<pre>= kp*(1-y(2))*(((2*f*kd*y(5))/kt)^0.5);</pre>				
55 -	ydot(3)	$= (4*kp*(1-y(2))*(((2*f*kd*y(5))/kt)^{0.5}))+((3*Mo*((kp*(1-y(2)))^{2}))/kt)+((2*f*io*y(2)))^{0.5}))/kt)$	(5)*kd)/Mo);			
56 -	ydot(4)	$= kd^{*}(1-y(4));$				
57 -	ydot(5)	= -(kd*io*(1-y(4)));				
58 -	ydot(6)	<pre>= ((2*f*kd*y(5)/kt)^0.5)+((kp*Mo*(1-y(2)))/kt);</pre>				
59						
60 -	ydot	<pre>= [ydot(1);ydot(2);ydot(3);ydot(4);ydot(5);ydot(6)];</pre>				
61						
				PSM_gel		

Figure A1 Continued

APPENDIX B – Execution of ODE Solver in Command Window



Figure B1 Execution of ODE Solver in Command Window