OPTIMIZATION STUDIES OF BATCH POLYMERIZATION FOR POLYSTYRENE PROCESS

by

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LIST OF ABBREVIATIONS

CVI	Control vector iteration
CVP	Control vector parameterization
DAE	Differential equation system
DOF	Degree of freedom
DYNOPT	Matlab dynamic optimization
HJB	Hamilton-Jacobi-Bellman
IAE	Integral of absolute error
LCH	Long chain hypothesis
MMA	Methyl Methacrylate
MWD	Molecular weight distribution
NE	Number of elements
NLP	Nonlinear programming
OC	Orthogonal collocation
ODE	Ordinary differential equation
ODE23	Ordinary differential equation of 2^{nd} /3^{rd} order Runge Kutta
P1	Objective function for minimize time

P2	Objective function for minimize initiator concentration
P3	Objective function for maximize conversion
P4	Objective function for maximize viscosity
PF1	Profit function 1
PF2	Profit function2
PMP	Pontragin's Minimum Principle
QSSA	Quasi-steady state approximation
R^2	Correlation coefficient
SOCOLL	Simultaneous optimization and collocation
SQP	Sequential quadratic programming
TP1	Customized temperature profile for constant temperature
TP2	Customized temperature profile for increasing temperature
TP3	Customized temperature profile for increasing and decreasing temperature
TPBVP	Two-point boundary value problem

LIST OF SYMBOLS

		Unit
$D_{m,n}$	Dead polymer of length m,n	-
$P^{\bullet}_{m,n}$	Macroradical of length m, n	-
$R^{\bullet}$	Primary radical	-
F_{Javg}	Average rate of coolant flow	L/hour
$O_P C$	Operating cost	RM
P_A	Price of reactant A	RM
P_B	Price of product B	RM
P_C	Price of by product C	RM
P_{FJ}	Cost of coolant	RM
V_r	Reactor volume	L
x_A	Mole reaction of reactant A	mole
x_{A0}	Mole fraction of reactant A at initial stage	mole
x_B	Mole fraction of product B	mole
x_C	Mole fraction of by-product C	mole
μ	Reactant viscosity	cp

μ_0	Zeroth moment of dead polymer distribution	-
μ_2	Second moment of dead polymer distribution	-
A_d	Frequency factor for initiator decomposition	1/s
A_p	Frequency factor for initiator propagation	1/(s mol)
A_t	Frequency factor for initiator termination	1/(s mol)
CC	Capital cost	RM
E_d	Activation energy for initiator decomposition	(kJ/(mol K)
E_p	Activation energy for initiator propagation	(kJ/(mol K)
E_t	Activation energy for initiator termination	(kJ/(mol K)
f	Initiator efficiency	-
I	Initiator concentration	mol/L
k_d	Kinetic constants for initiator decomposition	1/s
k_p	Kinetic constants for propagation	1/(s mol)
k_t	Kinetic constant for termination	1/(s mol)

M	Monomer concentration	mol/L
R	Gas constant	J/mol.K
S	Solvent molecule	-
T	Reactor temperature	^{o}C
t	Time process	hour
X	Monomer coversion	-

Greek Letters

$\mathcal{J}(.)$	Optimization criterion
$x(t)$	Vector of state variables
$u(t)$	Vector of control variables
p	Vector of time independent parameters
M	Constant mass matrix
$h(.)$	Equality design constraint vector
$g(.)$	Inequality design constraint vector
$x(t)^L, x(t)^U$	State profile bounds
$u(t)^L, u(t)^U$	Control profile bounds
p^L, p^U	Parameter bounds
$\varphi_j(t)$	Langrange function for the states variables
$\theta_j(t)$	Langrange function for the control variables
δ_{kj}	Kronecker delta

PENGOPTIMUMAN DINAMIK BAGI PEMPOLIMERAN BERKELOMPOK UNTUK PROSES POLISTERINA

ABSTRAK

Pempolimeran adalah satu proses tindak balas kimia bagi molekul monomer untuk membentuk rantai polimer. Dalam industri polimer, reaktor kelompok bagi pempolimeran digunakan secara meluas untuk menghasilkan polimer-polimer pelbagai gred. Proses kelompok mampu untuk mengendalikan variasi dalam stok suapan, spesifikasi produk dan corak permintaan pasaran. Ia juga sesuai untuk produk rendah-isipadu dan produk dengan pelbagai gred (seperti dalam polimer khusus), kerana setiap kelompok boleh dibuat mengikut resipi sendiri dan keadaan operasi tanpa menanggung kos. Walau bagaimanapun, proses ini mungkin memerlukan kos operasi yang lebih tinggi kerana ia boleh mencapai penukaran yang tinggi dengan masa kelompok yang panjang. Operasinya adalah tidak mantap di mana komposisi dan suhu sentiasa berubah dengan masa.

Keadaan operasi yang optimum adalah sangat penting untuk proses pempolimeran bagi mencapai fungsi objektif dalam proses. Dalam kajian ini, teknik pengoptimuman yang menggunakan model matematik telah dilaksanakan untuk mendapatkan syarat-syarat operasi yang optimum. Masalah pengoptimuman dinamik telah diselesaikan menggunakan kaedah kolokasi ortogon di mana pembolehubah pembezaan diasingkan sepenuhnya. Kaedah kolokasi adalah salah satu kaedah yang boleh digunakan untuk menyelesaikan pengoptimuman dinamik. Dalam kes menyelesaikan masalah pengoptimuman dinamik, formula kolokasi

boleh digunakan untuk mengubah persamaan pembezaan biasa ke persamaan algebra. Dalam kajian ini, pengoptimuman penghasilan suhu dalam proses kumpulan bagi polistirena telah dikaji secara teori. Sebab utama mengapa suhu telah dipilih sebagai pembolehubah yang optimum adalah disebabkan oleh kesan yang kuat ke atas penukaran monomer dan bilangan purata berat molekul. Pertama, model matematik untuk model tak-linear bagi proses reaktor dinamik telah dikaji. Kemudian, profil suhu optimum "off-line" telah ditentukan yang mana bergantung kepada produktiviti reaktor, kualiti produk akhir dan kekangan operasi akibat had proses.

Dalam kajian kes ini, model matematik bagi polistirena dan masalah pengoptimuman dinamik telah diselesaikan dengan menggunakan persekitaran MATLAB dengan menggunakan pakej kod "dynopt". Empat fungsi objektif telah dipertimbangkan dalam kajian ini: mengurangkan masa proses (P1), mengurangkan kepekatan pemula (P2), memaksimumkan penukaran monomer (P3) dan memaksimumkan kelikatan (P4). Daripada hasil simulasi, didapati bahawa fungsi objektif untuk mengurangkan masa proses (P4) telah dipilih sebagai operasi kawalan yang paling berkesan. Ia bergantung dari masa operasi minimum bagi penukaran monomer maksimum. Kemudian, kesan aspek-aspek yang berbeza seperti bilangan keadaan kolokasi, bilangan selang dan jenis trajektori untuk pengoptimuman proses ini juga telah dikaji.

OPTIMIZATION STUDIES OF BATCH POLYMERIZATION FOR A POLYSTYRENE PROCESS

ABSTRACT

Polymerization is a chemical reaction process of monomer molecules to form a polymer chain. In the polymer industry, batch polymerization reactors are used extensively to manufacture a variety of polymers of numerous grades. Batch process is well suited for low-volume products and for products with numerous grades (as in specialty polymers. However, this process may require higher operation cost because it can achieve high conversion with long batch time. The operation is unsteady-state where the composition and temperature always change with time. Optimum operating conditions are very important for the polymerization process in order to achieve the objective function in the process.

In this study, the optimization technique using mathematical models was implemented to obtain those optimum operating conditions. The dynamic optimization problem was solved using an orthogonal collocation method where the differential variables were fully discretized. Collocation method is one of the methods that can be used to solve dynamic optimization. In the case of solving the dynamic optimization problems, collocation formulae can be used to transform the ordinary differential equations into algebraic equations. In this study, the optimization of optimal temperature generations in batch process of polystyrene was investigated theoretically. The main reason why temperature was chose as optimal variable is due to its strong effect on the monomer conversion and number-average

molecular weight. First, the mathematical model for non-linear model of reactor dynamics of the process was investigated. Then, off-line optimal temperature profile was determined which depends on the reactor productivity, the quality of final product and operating constraints resulting from process limitations.

In this case study, the mathematical model of the polystyrene and the dynamic optimization problems were solved using the MATLAB environment by using *dynopt* code package. Four objective functions were considered in this study: minimize process time (P1), minimize the initiator concentration (P2), maximize monomer conversion (P3) and maximize viscosity (P4). From the simulation result, it was found that the objective function for minimize process time (P1) was chosen as the most effective control operation. It depended from a minimum time operation for maximum monomer conversion. Then, the effect of different aspects such as number of state collocation, number of intervals and type of trajectory for this optimization process was also studied.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Polymerization is a reaction process of monomer molecules together in a chemical reaction to form polymer chains. There are many types of polymers including synthetic and natural polymers. Polystyrene is one of synthetic polymer that can be recycled. It is used extensively for low-cost applications due to inexpensive and easy process ability. Besides, it is a typical rigid plastic which is a good electrical insulator and has excellent optical clarity due to lack of crystallinity. It is also has possesses good resistance to aqueous acids and bases and easy to fabricate into products. Due to the excellent properties described above, polystyrene is now used in electrical/electronic, automotive, and industrial films applications. It also has been very successfully used in packaging, building and construction, and in injection moulding applications.

Generally, high impact polystyrene can be produced with two basic methods which either by using batch process or continuous process. There are a few major aspects that show the differences between batch process and continuous process. First different between the batch and continuous process is the mode of operation. In batch process, the mode of operation is intrinsically dynamic where the operating conditions are time varying. Second aspect is the role of initial loading. The role of initial

conditions is very important in batch process as compared to the continuous process, the loading conditions become a major operational issue when there is a possibility for multiple steady states to exist. The third aspect is that the batch process has more flexibility of operation and ability to cope with the fluctuation of market conditions. Batch process is usually used in small-volume production such as in pharmaceuticals and other fine chemicals with limited batch cycle time. It is more difficult to control the operating conditions of batch process due to the wide range of operation. Besides that, the batch process model requires more accuracy than continuous process model. Batch process has irreversible behavior which means that it may be no means for any correction if once off-specification material is produced because of an upset in the operating conditions. This may need the process shutdown and discard of the reaction mixture. However in a continuous process, the upsets in operating conditions actually wash out of the system and the process can return back to the desired steady state conditions.

Polymerization reactors is very difficult to control and measure because of the complexity of the physical mechanisms and polymerization kinetics. This is due to many important variables cannot be measured on-line and only can be measured at low sampling frequencies. The important variables are related to end-use polymer properties which are the main factor for determining the entire molecular weight, copolymer composition, sequences length and branching distributions. In general, the major objective of optimization is not to keep the system at a set point but to achieve a desire variable at the end of the batch cycle.

Normally, optimization process is used for improving the product quality, reducing product variability, reducing production costs, and meeting safety requirements and environmental regulations. There are a lot of different types of optimization methods and problems but each of the optimization problems usually have a great deal in common of an objective function, constraints and choice variables. Besides, there are two major types of optimization problems in polymerization process. First, the selection of the best (optimal) time invariant controls which is without disturbances, the final product will attains the desired molecular and morphological properties. A second different aspect is time optimal control problem. This problem deals with the calculation of time-optimal control trajectory to ensure that the requirements of polymer quality and the operational process constraints are satisfied. Besides, these optimal control policies can be calculated off-line and implemented as set point changes of the regulatory process controllers (Ozkan et al., 1998)

Nowadays, Orthogonal Collocation is one of the most popular method used because optimal control problems or differential algebraic optimization problems cannot be solved by using straightforward nonlinear programming techniques or optimal control methods since the optimization of continuous profiles is an infinite dimensional problem. Riascos and Pinto (2002), Krallis et al., (2006) and Ruppen et al., (1995) used orthogonal collocation method to solve their optimization problem. Based from their work, they found several advantages by using this method. Riascos and Pinto (2002) applied this method to simplify fed-batch biochemical reactor which is a process of biosynthesis of penicillin from glucose and to discrete differential equations systems

(DAE). From their observation, this method efficiently transforms dynamic optimization problems into nonlinear programming (NLP) problems and it is enable to solve complex problems with several control variables and minimizing the approximation error. Moreover, Ruppen et al., (1995) concluded that by using this method, user is more easily to include any type of algebraic path or endpoint constraints and can use a computationally-attractive simultaneous solution and optimization approach.

1.2 Problem Statement

There are many parts of polymerization process with involve processes which can exhibit highly nonlinear dynamic behavior phenomena such as multiple steady states, sustained oscillations and traveling waves. Furthermore, polymerization reactor is difficult to control due to lack of on-line process control sensors to measure polymer properties. Based on that, the operation and economic of polymer plant can be improved by the development and application of state estimation, process optimization and advanced process control.

There are a lot of different types of optimization methods and problems but each of the optimization problems usually have a great deal in common of an objective function, constraints and choice variables. There are two popular approaches which are usually used to solve differential algebraic optimization problems. The first one is the sequential method or control vector parameterization. This method discretizes only the

control variables, and the differential equations systems (DAE) is integrated using standard integration algorithms. The optimization is carried out in the space of decision variables. The second method often used discretized all variables that converts the dynamic optimization problems into nonlinear programming (NLP) which is called as simultaneous method. In this method, the optimization is carried out in full space of the discretized variables and enables the solution of problems with constraints on the state and control variables. Unfortunately, the first method can be prohibitively expensive even for small problems as it tends to converge slowly and require solution of differential equations at each iterations.

Dynamic optimization is often used in order to find the optimal control profile of one or more control variables or control parameters of a system. Optimality is defined as the minimization or maximization of an objective function without violating the given constraints. Solving the dynamic optimization problems directly (analytically) is not easy and an impossible task for large scale systems. Several methods have been developed in order to solve dynamic optimization problems with a full discretization of state and control variables. Collocation method is one of the methods that can be used to solve dynamic optimization. The reason is that in the case of solving the dynamic optimization problems, collocation formulae can be used to transform the ordinary differential equations into algebraic equations. Nowadays, the Orthogonal Collocation is one of the most popular methods used due to its optimal control problems or differential algebraic optimization problems which cannot be solved by straightforward

nonlinear programming techniques or by optimal control methods since the optimization of continuous profiles is an infinite dimensional problem.

Thereby, the orthogonal collocation method combined with a non-linear programming method (i.e. sequential quadratic programming (SQP)) is used to solve the dynamic optimization problem. SQP algorithm can linearize inequality and equality constraints and constructs objective function from gradients of the objective and constraint functions. Previous study showed that the discretization of DAE by orthogonal collocation in finite elements efficiently transforms the dynamic optimization problems into NLP problems. Optimization with orthogonal collocation method also has a great advantage since it reduces the computational effort in terms of calculation time. This is a good advantage when using the algorithm to recalculate the trajectory of the process if the optimum temperature of reactor carried out differs from the optimal temperature of reactor calculated previously.

1.3 Research Objectives

The objectives of this study are:

i. To use and validate a first principle model of the polymerization batch process for polystyrene for use in optimization process.

ii. To study the effect of reactor temperature and initial concentration to the production of polystyrene in batch reactor.

iii. To develop procedure of calculating optimal temperature profile using Orthogonal Collocation method.

iv. To use model of the process for optimizing the optimal temperature profile

v. To study the effect of different aspects of optimization towards batch polymerization of polystyrene process.

1.4 Organization of the thesis

There are 5 chapters divided in this thesis. Each chapter gives specific information about this project.

Chapter 1

This chapter introduces the general knowledge about the polymerization process and also polystyrene process specifically. It also gives an overview of process optimization used nowadays. In addition, the problem statement and objective of this research project also stated in this chapter.

Chapter 2

This chapter gives literature review of the polymerization process especially in polystyrene. It also reviews a mathematical models and the optimization method used in several research project. Finally, current application of dynamic optimization and orthogonal collocation method are reviewed here.

Chapter 3

This chapter describes the methodology of this research. The first section presents the assumptions and mathematical expressions of mass balance and energy balance in the polystyrene process used. Then, it also mentions the list of important parameters chosen for the objective function study. Finally in this chapter, the dynamic optimization study procedure is explained.

Chapter 4

This chapter presents the result and discussion of this research. The first part of this chapter contains the result and discussion for kinetic study used and validation of the result using basic ordinary differential equation (ODE), the effect of reactor temperature and initial concentration towards process time and monomer conversion. The results of the dynamic optimization study of four different objective functions are evaluated and compared in the following part. The final part of this chapter presents the effect of different aspects of optimization such as number of state collocation, number of intervals and type of trajectory in the objective function.

Chapter 5

This chapter summarizes all the results obtained in the present study and also highlights some recommendations for future studies.

CHAPTER 2

LITERATURE REVIEW

This chapter presents the literature review of previous studies of the batch reactor and polymerization process. Various approaches and methods that are currently used to model and optimize batch polymerization reactor were also described in this chapter. Finally, it also reviews the optimization method used in several research projects.

2.1 Polymerization

Polymerization is a process where the reacting monomer molecules are together in a chemical reaction to form polymer chain. Polymerization is carried out by two major classes of mechanisms: (Ray and Villa, 2000)

i) Addition polymerization in which monomer units are added to the growing chain one at a time

ii) Condensation polymerization in which the chains themselves react with each other to increase the chain length.

Usually in dynamics process, condensation polymerization is not a great interest due to smaller heat of polymerization. Unlike the condensation polymerization, the addition polymerization reactions are always highly exothermic and dynamics.

In general, polymerization process can be classified into homogeneous and heterogenous. In homogeneous systems, polymerization is carried out in a single phase. On the other hand, for heterogeneous system, the polymer is insoluble in the monomer phase or the polymerization involves the presence of different phase. There are eight different polymerization processes; i) bulk, ii) solution, iii) precipitation, iv) suspension, v) emulsion, vi) solid catalyzed polymerization vii) interfacial polycondensation, and viii) solid state.

Styrene is a typical example of monomers where the bulk polymerization is homogeneous. In bulk polymerization, the feed to the reactor consists essentially of pure monomer with small amounts of dissolved catalyst and it can be either homogeneous or heterogeneous type depends on the mutual solubility of monomer and polymer. Basically, in homogeneous bulk polymerization, the process has high viscosity of reaction mixture and poor heat transfer characteristics. At intermediate conversions, the rate of heat generation often accelerates with conversion (due to gel effect). Thus, it becomes impossible to carry out the reaction beyond 50% conversion. (Ghasem *et al.,* 2007)

2.2 Polystyrene

Polystyrene is one of the most widely used plastics nowadays. It was discovered in 1839 by Eduard Simon, an apothecary in Berlin. Structurally, it is a long hydrocarbon

chain, with a phenyl group attached to every other carbon atom. The polystyrene is produce by a free radical vinyl polymerization which is from the monomer styrene.

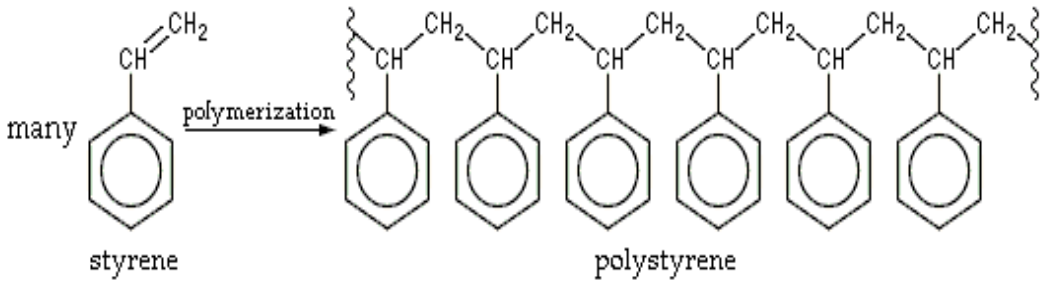

Figure 2.1: Polystyrene formation

Polytyrene is a thermoplastic substance which normally exists in solid state at room temperature, but melts if heated (for molding or extrusion), and become solid again when cooling off. Pure solid polystyrene is a colorless and hard plastic with limited flexibility. In order to increase the utility of styrene products, copolymerization and polymer blends are usually used. Copolymerization is polymerizing a mixture of two monomers. The product has been referred as a copolymer which contains both monomers in polymer chain. Whereas, polymer blends are a physical mixture of two different materials (either homopolymers or copolymers)

Polystyrene is used extensively for low-cost applications because it is inexpensive and easy process capability. Besides, it is a typical rigid plastic and a very good electrical insulator, excellent optical clarity due to the lack of crystallinity, possesses good resistance to aqueous acids and bases and it is easy to fabricate into products. Due to the excellent properties described above, polystyrene is now used in

electrical/electronic, automotive, and industrial films applications. It is also has been very successfully used in packaging, building and construction, and in injection moulding applications.

2.3 Batch Reactor

Mostly in polymerization, batch reactor is widely used in this process. Batch reactor is an essential unit operation used in almost all batch processing industries. Figure 2.1 shows a schematic diagram of a batch reactor. Typical batch reactor consists of a tank with agitation and recirculating heating-cooling jacket fluid to maintain the temperature within a desirable range. In batch reactor, while the reaction is carried out, no inflow or outflow of reactants or products into a vessel and it is left to react for a certain period. Then after completed the process, the products are discharged. This process may require high operation cost per unit production because it can achieve high conversion with long batch time. Therefore, it is not feasible for large scale production. (Aziz and Mujtaba 2002).

Extensively in the industry, batch reactors are almost used for small scale operation for testing new processes that have not been fully developed, for the manufacturing of a variety of polymers of numerous grades and for processes that are difficult to convert to continuous operation. It is also well suited for low-volume, high value products such as pharmaceuticals, polymers, biotechnology or other fine chemicals product. Batch reactor is almost used for testing for processes that are

difficult to convert to continuous operation, when they are many processing steps in the chemical process, when isolation is required for reasons of sterility or safety and when materials involved are difficult to handle. (Palanki et al., 1993)

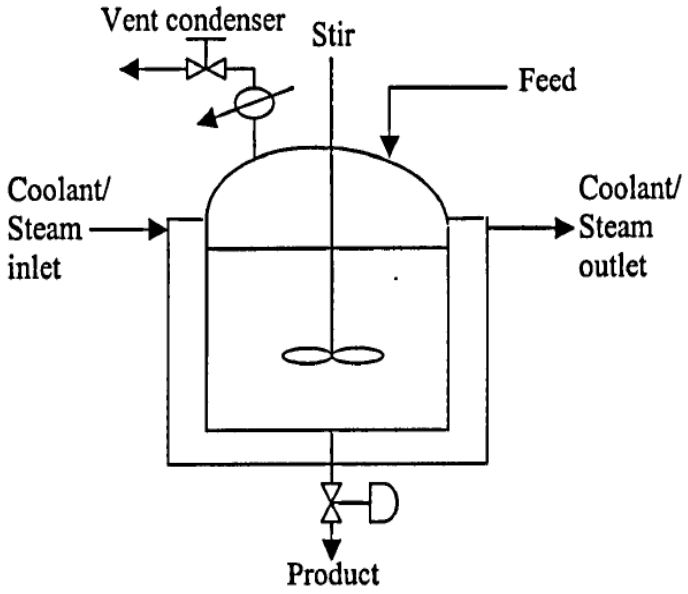

Figure 2.1: A schematic diagram of a batch reactor (Aziz and Mujtaba 2002)

There are a few major aspects that show the different between batch processes and continuous processes. First is the mode of operation. In batch process, their mode of operation is intrinsically dynamic which is where the operating conditions are time varying. Second aspect is role of initial loading. The role of initial conditions is very important in batch processes compared to in continuous processes, the loading conditions become a major operational issue when there is a possibility for existence of multiple steady states. The third aspect is batch process has more flexibility of operation

and ability to cope with the fluctuation of market demand (Freidrich and Perne,1995, Karagoz *et al*., 2000, Qian *et al*. 2009 Ge *et al*., 2000).

The operating conditions of the batch process is difficult to control because it has wide range of operation. Besides that, the batch process model requires more accuracy than continuous process model. Batch processes have irreversible behavior which means they may be no means for any correction if once off-specification material was produced because of an upset in the operating conditions. This may need the process shutdown and discard of the reacting mixture. However in continuous processes, the upsets in operating conditions actually wash out of the system and the process can return back to the desired steady state conditions (Soroush and Kravaris, 1993, Ozkan *et al*., 1998, Ekpo and Mujtaba, 2007).

2.4 Optimization

The optimization of batch process has attracted attention in recent years. The major objective of modeling polymerization reactor is to understand how the kinetic mechanism, the physical transport phenomena, mixing, reactor type and operating conditions affect the product quality. It is because the product quality is the main target in polymer manufacturing. By using process modeling, optimization and control on polymer plant operability and economics, a significant impact for the whole process especially on product quality can be obtained (Kiparissides, 2006).

Polymerization reactors is very difficult to control and measure due to the complexity of the physical mechanisms and polymerization kinetics. This is because many important variables cannot be measured on-line and only can be measured at low sampling frequencies. The important variables are related to the end-use of polymer properties which is the main factor to determine the entire molecular weight, copolymer composition, sequences length and branching distributions. (Richards & Congalidis, 2006). In a polymerization production, it is desirable to produce polymer with best properties at lower cost. In a batch process, the productivity can be increased by decreasing the batch time while still maintaining molecular weight distribution of the final polymer in the desired range.

There are lots of different types of optimization methods and problems but each of the optimization problems usually have a great deal in common of an objective function, constraints and choice variables. Besides, there are two major types of optimization problems in polymerization process. First is the static optimization problem which it is the selection of the best (optimal) time invariant controls so that without disturbances, the final product will attain the desired molecular and morphological properties. The second type is time optimal control problem refers to the determination of the optimal control trajectories to ensure polymer quality requirements and the operational process constraints are satisfied. Besides, these optimal control policies can be calculated off-line and implemented as set point changes of the

regulatory process controllers (Ozkan et al., 1998). Static optimization is usually related to the steady state operation of continuous polymers reactor while the second type is concerned with the dynamic operation of batch and semi batch reactors.

There are four general steps solutions in the optimization problems (Kiparissides, 1996). The first step in the analysis and optimization of a polymer reactor is the development of an accurate model of the process. Second step is the selection of the control variables. In polymer reactor, the molecular properties of a polymer will depend on a number of control variables. Two types of control variable mostly used are reaction variables and initiator variables. The final selection of the control variables will depend on the specific design of the polymer reactor, its operational mode, the sensitivity of the polymer properties to manipulate the control variables and the optimization objectives. Next is the definition or selection of the objective function. In general, the optimization objectives will fall into the following categories. There are molecular property specifications, safety, reactor and environmental constraints and economic objectives. Last step is the suitable selection of numerical method for solving the specific optimization problem.

Table 2.1 lists papers recently published on the application of optimal control theory to batch reactors. Recently there are many papers published the application of optimal control theory to polymerization reactors. Louie and Song (1975) reviewed on optimal control polymerization reactors and studied different strategies for

minimization of polymer polydispersity by manipulating the reactor temperature, monomer and solvent feed rates and rate of initiation. They concluded that the manipulation of solvent addition would give better result but slightly longer reaction times. Meanwhile multi objective optimization has been studied by Tsoukas *et al.,* (1982), Cawthon and Knaebel (1989) and Butala *et al.,* (1992). The desired on this optimization is to control the monomer conversion, copolymer composition and molecular weight distribution simultaneously in a minimum batch time. They have shown that the results obtained were better than the results from previous research.

Takamatsu *et al*.,(1988) studied the molecular weight distribution (MWD) control in a batch reactor for requirement of producing high-quality polymers. To get the desired MWD, they used two-step method to obtain trajectories of the reactor temperature and initiator concentration. The first step of the two-step method given is to obtained profiles of the instantaneous of average chain length and polydispersity which has three types of solution. For the first type, they solved it by using rectangular type, the type two of solution is by using the second order polynomial of moment of the concentration of dead polymer and the last one is type three which is using mixed type of zero-and-first order polynomial of moment of the concentration of dead polymer solution. The second step is to calculate the operating conditions of temperature and initiator concentration for all types of solutions in the first step. Amongst the three types of solutions, type three is chosen because it has indicated that the time profile of the reactor temperature is continuous and it is more sensitive to the disturbance of overall heat-transfer coefficient compared to the other two types.

However, Chang and Lai (1992) have calculated the procedure to estimate the time profile of temperature for MWD control using modified two-step method. This method also can determine initiator concentration in a general free radical polymerization batch reactor. Comparison between these methods and original two-step method showed that this method can avoid the complicated numerical computations required to solve the nonlinear algebraic equations for Methyl Methacrylate (MMA) bulk polymerization batch reactor. They also showed that this procedure is very flexible because it can use this calculation procedure in different mathematical model and it is also accurate and effective.

Aziz and Mujtaba (2002) formulated the optimization problems for batch reactors with design, operation and environmental constraints. The main objective of this research is to select a suitable and efficient method from the existing technique to solve two different types of optimization problems which are maximum conversion and minimum time problems. They optimized the decision (optimization) variables with only discretise the control variables u(t) using control vector parameterization (CVP) method. This technique posed the dynamic optimization problems as a nonlinear programming (NLP) problem and solved it using a successive quadratic programming (SQP)-based optimization technique. CVP technique is proved to be able to handle large systems without the need to solve excessively large optimization problem and also able to solve the minimum time optimization problem. However, this method also can be prohibitively expensive even for small problems because it tends to converge slowly and require solution of differential equations at each iteration. (Biegler, 1984).

Ozkan *et al*., (2001), Karagoz *et al*., (2000) and Ghasem *et al*., (2007) evaluated the optimal temperature profiles which the reactor should produce the desired polymer product with 50% conversion and 500 numbers of average chain lengths in a minimum time using Hamiltonian optimization method. They also assumed that constant density, no-chain transfer and quasi steady-state approximation for kinetic models in a batch reactor to be used in mathematical model. Optimal trajectories were calculated based on total simulation program which has the mass and energy balances of the jacketed polymerization reactor. The reason why they had chosen temperature as an optimizing variable is because temperature has strong effect on the monomer conversion and number-average molecular weight which is a desired property. Furthermore, optimal temperature profiles were obtained by applying the maximum principle to the mathematical model to produce the desired polymer properties.

Araujo and Giudici, 2003 used Iterative Dynamic Programming (IDP) method to optimize of semicontinuous emulsion polymerization reactions. The optimization was applied in order to minimize the reaction times, the time intervals with varying lengths were used to obtain desired properties. IDP was showed to be a straightforward procedure that allows the implementation of optimization constraints and to optimize highly complex and nonlinear equation systems. The results show that the optimization procedure was able to minimize the reaction time and, simultaneously, obtaining a polymer with a desired quality (composition or molecular weight).

Nowadays, Orthogonal Collocation is the one of the most popular method used in optimization. Orthogonal collocation method is popular because the optimal control problems or differential algebraic optimization problems cannot be solved by straightforward nonlinear programming techniques or by optimal control methods since the optimization of continuous profiles is an infinite dimensional problem (Riascos and Pinto, 2002, Krallis *et. al*., 2006, Ruppen *et al*. 1995). They used orthogonal collocation method to solve their optimization problem. Based from their work, they found several advantages by using this method. Riascos and Pinto (2002) applied this method to simplified fed-batch biochemical reactor which is a process of biosynthesis of penicillin from glucose and to discretize differential equations systems (DAE). From their observation, this method efficiently transforms dynamic optimization problems into nonlinear programming (NLP) problems and it enable them to solve complex problems with several control variables and minimizing the approximation error. Moreover, Ruppen *et al*., (1995) concluded that by using this method, the user can easily include any type of algebraic path or endpoint constraints and can use a computationally-attractive simultaneous solution and optimization approach.

Optimal control study using orthogonal collocation method has also been studied by Jang *et al.*,(1993). They developed the experimental and theoretical initiator feed and temperature profiles in order to reach specified average molecular weight and conversion in a minimum time using MMA polymerization process reactor. The result showed that a good agreement has been reached between experimental and theoretical results. They also concluded that optimal policies are generally have no value if

constraints are not taken into consideration and the optimal operation time is usually much longer than the predicted when constraints are not considered.

Biegler (1983) has applied orthogonal collocation to the system of differential equations and converted them into algebraics that are simultaneously converging to the optimum while solving the differential equations. In this study, the simultaneous optimization and collocation (SOCOLL) method was compared with the control vector iteration (CVI) and control vector parameterization (CVP) method. Based on the result, the SOCOLL strategy handles ODE without difficulty compared to the other two methods. This could be due to the fact that the CVI and CVP methods tend to converge slowly and require solution of differential equations at each iteration.

There is another paper that studied the optimization using collocation method. The objective of this paper is to make comparison between a global end-point collocation method with SOCOLL (Simultaneous Optimization and Collocation) method for solving dynamic optimization problems in order to examine whether the end-point included to provide any improvement or not to the solution. The end point collocation method is different from the SOCOLL method in that the endpoint at t_f is also a collocation point. It is because if the end-point is not used, then extrapolation equations for the state variables must be included in the problem formulation. They also investigated the effects of the number of interior collocation points and the collocation methods. The result showed a non uniform improvement with respect to the increasing

collocation points between these two methods. However, one of the criteria to choose which one is the best method is that the method must gives the best overall fit of the approximate to the simulation state profiles or which one gives the lowest value of integral of absolute error (IAE). Based on the statement, it showed that the end-point collocation method is the best method compare to SOCOLL method because the IAE is smaller for in all three cases. (Tieu *et al*., 1995 and Costa *et al., 2003*).

2.5 Mathematical modeling

2.5.1 Effect of initiator concentration and reactor temperature in polymerization process

Basically in batch polymerization process, the main optimizing variable is temperature reactor because it has a strong effect on the polidisperty, monomer conversion and weight-average molecular weight. The second variable usually used as optimizing variable is initiator concentration (Soroush and Kravaris, 1993). On the other hand, there are several ways to minimize batch time in polymerization process. The two popular methods are by raising the reaction temperature or adding more initiator into the system. However, both methods will reduce the molecular weight. Using more initiator will leave a larger amount of undecomposed initiator which is costly to be removed and also an environmental hazard. It will increase the product cost. (Gao *et al.,* 2004)

A number of studies have been reported in the literature on the optimization of polymerization systems. Most of the studies are consider two of the following aims as a objective functions. There are minimization of the reaction time, reduction of the monomer and initiator residue concentration in the product and maximization of the monomer conversion. The operating variables usually manipulated include the reaction temperature, initiator addition and monomer feed rate (Silva and Biscaia, 2003). Karagoz *et al.,* (1999) and Zeybek *et al.,* (2006) optimized the temperature profiles at different initiator concentration to produce polymer with the desired properties in a batch polymerization of styrene. This study was applied experimentally and theoretically. The calculation of optimal temperature profile was carried out to obtain the required final monomer conversion and number average value of molecular weight in a minimum reaction time. They concluded that by using more initiator will decrease the reaction time. However, by increasing the initiator concentration, it will decrease the molecular weight.

2.5.2 Viscosity

Erdogan *et al*., 2002 investigated experimentally the effect of operational conditions on the performance of a controlled batch reactor. In the reaction, the viscosity of the reacting mixture is measured continuously by using a falling ball viscometer.