OPTIMIZATION OF EMULSION POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE (MMA)

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

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SUPERVISOR’S DECLARATION

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

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Date : JANUARY 2013

STUDENT’S DECLARATION

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

Signature	:	
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Date	:	JANUARY 2013

Special **dedication** *to my supervisor, my family members,*

my friends, my fellow colleague and all faculty members
for all your care, support and believe in me.

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A_s	area of one surfactant molecule taken up when adsorbed onto a surface, dm^2
A_{tot}	total surface area of latex particles, dm^2
B(V ,V)	coagulation rate coefficient of two particles of volume V and V’, $Lmol^{-1}s^{-1}$
$C_{micelle}$	concentration of micelles, mol L−1
C_P	concentration of monomer in the latex particles, mol L^{-1}
C_{P_sat}	concentration of saturated monomer in the latex particles, mol L^{-1}
C_W	concentration of monomer in the water phase, mol L^{-1}
C_{pm}	heat capacity of themonomer, J/g ◦C
C_{pw}	heat capacity of water, J/g◦C
d_m	density of monomer, kg L^{-1}
d_p	density of polymer, kg L^{-1}
D_W	coefficients of diffusion for monomer in water,dm^2
e	error
[E]	concentration of desorbed radicals in aqueous phase, mol L^{-1}
F_m	rate of monomer to the reactor, mol s^{-1}
$F_{m,in}$	feed rate of inlet monomer, mol s^{-1}
G	number of radial intervals into which the particle size distribution is split
$[IM_i]$	concentration of oligomeric radicals of degree ‘i’ in aqueous phase, $molL^{-1}$
j_{crit}	polymerization critical degree for homogeneous nucleation
K	propagation volume growth rate per particle,Ls^{-1}
k_d	initiator decomposition rate coefficient, s^{-1}
k_{dM}	desorption of monomeric radicals from particles rate coefficient, s^{-1}
k_e^i	rate coefficient for entry of an oligomeric radical of degree ‘i’ into an existing particle, $Lmol^{-1}$ s^{-1}

k_{eE}	rate coefficient for re-entry of desorbed radicals, $\mathrm{Lmol^{-1}\ s^{-1}}$
$k_{e,micelle}^{i}$	rate coefficient for entry of an oligomeric radical of degree ‘i’ into a micelle, $\mathrm{Lmol^{-1}\ s^{-1}}$
k_p	long chain limiting propagation rate coefficient in the latex phase, $\mathrm{Lmol^{-1}s^{-1}}$
k_p^1	monomeric radical propagation rate coefficient in the latex phase, $\mathrm{Lmol^{-1}\ s^{-1}}$
$k_{p,aq}^{i}$	aqueous phase propagation rate coefficient for oligomeric radicals of degree ‘i’, $\mathrm{Lmol^{-1}\ s^{-1}}$
k_{mwp}	Partition coefficient for styrene between the water phase and polymer phase
$k_{t,aq}^{i,j}$	rate coefficient for termination reaction between oligomeric radicals of degree ‘i’ and ‘j ’in the aqueous phase, $\mathrm{Lmol^{-1}\ s^{-1}}$
k_{tr}	radical transfer to monomer rate coefficient, $\mathrm{Lmol^{-1}\ s^{-1}}$
M_o	monomer molecular weight, $\mathrm{kgmol^{-1}}$
$\tilde{n}$	average number of radicals per particle
n(r)	molar concentration density of particles of unswollen radius r, $\mathrm{molL^{-1}dm^{-1}}$
$n_o(r)$	molar concentration density of particles of unswollen radius r containing no radicals, $\mathrm{mol\ L^{-1}\ dm^{-1}}$
$n_1^M(r)$	molar concentration density of particles of unswollen radius r, containing monomeric radicals, $\mathrm{mol\ L^{-1}\ dm^{-1}}$
$n_1^P(r)$	molar concentration density of particles of unswollen radius r, containing polymeric radicals, $\mathrm{mol\ L^{-1}\ dm^{-1}}$
N_A	Avogadro’s constant, $\mathrm{mol^{-1}}$
N_m	number of moles of monomer
$N_{m,T}$	total number of moles of monomer
N_{tot}	total number concentration of particles, $\mathrm{L^{-1}}$
r	latex particle radius, dm
Δr	radial interval size, dm
<r>	number means particle radius, nm
$<r^2>$	number means squared radius, $\mathrm{nm^2}$
R_P	polymerization reaction rate, mol L−1 s−1

R_{pAp}	polymerization rate of monomer A in the particle phase
R_{pAw}	polymerization rate of monomer A in water phase
r_s	swollen radius of latex particle, dm
S	concentration of added surfactant per unit volume of the aqueous phase, mol L−1
S_W	concentration of free surfactant in the aqueous phase, mol L−1
T_{reac}	reaction temperature, ◦C
V_M	monomer volume in the system, L
V_P	polymer volume in the system, L
V_r	total reaction volume, L
V_W	water volume in the system, L
X	instantaneous monomer conversion
z	critical degree of polymerization for entry

PENGOPTIMUMAN BAGI METHYL METHACRYLATE DAN STIRENA EMULSI POLIMERISASI

ABSTRAK

Karya ini mengkaji pengoptimuman bagi Stirena dan metil metakrilat (MMA) emusi polymerisasi. Satu rangka kerja yang berasaskan model bagi operasi optimum proses pengkopolimerisasi telah digunakan dalam persekitaran gPROMS dan membolehkan kita untuk meramalkan penukaran monomer maksimum. Kerumitan proses diwakili oleh model matematik untuk pengoptimuman dan kawalan. Satu model proses yang melibatkan persamaan bagi jisim dan keseimbangan tenaga menerangkan evolusi zarah dalam reaktor berkelompok dan kinetik penyebaran dikawal dimasukkan ke dalam rangka kerja pengoptimuman. Model adalah akaun untuk fizik-kimia kompleks sub-proses yang melibatkan mekanisme pembentukan partikel dengan dua titisan monomer, surfaktan, pemula dan zarahan. Menggunakan gPROMS, sistem dianalisis data, dicipta model, algoritma maju, dimanipulasi dan diplotkan berdasarkan fungsi dan data. Penentuan profil optimum untuk pembolehubah kawalan yang digunakan untuk pempolimeran emulsi stirena dan MMA yang menghasilkan penukaran dikehendaki dengan masa kumpulan tetap dan nombor tetap purata berat molekul dalam reaktor kelompok masing-masing telah dijalankan di dalam reaktor kelompok. Pengurangan masa pra-kumpulan meningkatkan Mn tetapi mengurangkan penukaran (X_n). Lebih cepat penambahan monomer ke dalam reaktor, awal pertumbuhan rantai polimer yang membawa kepada yang lebih tinggi Mn. Kenaikan suhu tindak balas akan mengurangkan M_n sejak kenaikan suhu akan meningkatkan kadar tindak balas penamatan.

OPTIMIZATION OF EMULSION POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE (MMA)

ABSTRACT

This paper studies the optimization of emulsion copolymerization of Styrene and Methyl Methacrylate (MMA). A model-based framework for optimal operation of copolymerization processes was used in gPROMS environment and enables us to predict the maximum monomer conversion for a given total monomer feed over the batch time. The complexities of the process were represented by mathematical models for optimization and control. A process model involving the equations for mass and energy balance describing the particle evolution in a batch reactor and diffusion controlled kinetics is incorporated into the optimization framework. The modeling is account for complex physic-chemical sub-processes involving particle formation mechanisms with two monomer droplets, surfactants, initiator and particulates. Using gPROMS, the system analyzed the data, created models, developed algorithms, manipulated and plotted based on the functions and data. The determination of optimal profile for control variables used for emulsion polymerization of styrene and MMA that yielded desired conversion with fixed batch time and fixed number average molecular weight in batch reactor respectively were carried out in batch reactor. Reduction of the pre-batch time increases the M_n but decreases the conversion (X_n). The faster the addition of monomer into the reactor, the earlier the growth of the polymer chain leading to higher M_n. The increases of the reaction temperature will decrease the M_n since increases of temperature will increase the rate of termination reaction.

CHAPTER 1

INTRODUCTION

1.1 Background of the proposed study

Emulsion polymerization is an important industrial application. This process widely used to produce a variety of polymers of multiple uses, for examples paints, adhesives, coatings, varnishes, SBR rubber, and PVC “paste” polymers. The molecular weight distribution (MWD), polymer microstructure, glass transition temperature (T_g), particle size distribution (PSD) and particles morphology are the factors that may affect the properties of the product. In order to produce specific latex particles with certain properties, all these parameters must be included in the process design and optimization as well as control (B.Benyahia, 2010).

Emulsion polymerization is a technique leading to colloidal polymer particles dispersed in a continuous medium, most often water. It is a free radical polymerization carried out under heterogeneous conditions. The origin infinite dimensional problem can be in principle transformed to nonlinear (NLP) problem and solved by using gPROMS software (R.Paulen, 2010).

1.2 Problem Statement

Engineers always seek new ways to obtain the polymers with prescribed end-use properties with high productivities and low cost in industry. During manufacturing processes, the optimization is a way to solve the problem domain with all those goals and constraints and get the best and optimal results. Software optimization is the process of modifying a system to make some aspect of it work more efficiently or use fewer resources to lower the operation costs in the plants. In this study, gPROMS is used to build, simulate as well as optimize the model.

There is much limiting in modeling, the control of emulsion polymerization is a challenging. In polymer industry, usually manufacturers must produce their specific polymer in its final form and shape for their intended application. This study is studying the optimization of emulsion copolymerization of styrene and methyl methacrylate (MMA) in batch process. A model was developed in the gPROMS software to describe the complete patterns of the emulsion polymerization and the monomer conversion (X_n) was optimized at the end of this work.

1.3 Research Objectives

This study outlines the following objectives:

i. To determine the maximum monomer conversion of copolymerization of Styrene and MMA for a given total monomer feed over the batch time.

ii. To determine the number average molecular weight of copolymerization of Styrene and MMA for a given total monomer feed over the batch time.

1.4 Scope of Proposed Study

The purposed study is to

- Find the optimum conversion of emulsion copolymerization of Styrene and Methyl Methacrylate (MMA) at a given total monomer feed while respecting these constraints.
- gPROMS software was used to develop a model of emulsion polymerization.
- Monomers used in the polymerization process are Styrene and MMA
- The initiator used in the process is Potassium Persulfate ($K_2S_2O_8$).
- The surfactant used in the process is Sodium Decoeyl Sulfate (SDS).

1.5 Expected Outcome

The dynamic optimization problems are transformed into nonlinear programming problem (NLP) using the CVP techniques which are solved using gROMS. An emulsion copolymerization of styrene and MMA was developed in the gPROMS and the monomer conversion of copolymerization of styrene and MMA for a given total monomer feed over the batch time was determined. gPROMS was chosen as simulation tools to optimize the model as it is expected can be simulating well with all the data without further complexity of equations. The product quality variables copolymer composition will be controlled in this work too.

1.6 Significance of Proposed Study

Molecular weight is one of the main factors which can affect an entire polymerization process as it is related to the mechanical and end use properties of the polymer itself. By maximizing the overall conversion, the downstream separation process cost can be minimized. Apart from that, this study is able to get a better design of emulsion polymerization.

Emulsion polymerization process is a technologically and commercially important synthesis process. Every annual, millions of tones of polymers are prepared by this synthesis process. It is continues to expand because of versatility of the reaction and greater realization of the ability to control the properties of the polymer latexes produced. Better design of emulsion polymerization offers great promise for the synthesis of materials. Furthermore, by optimize the molecular conversion, a better quality of product can be produced. Lastly, this study via the gPROMS work is also able be designed to consume less energy, and less cost of operating production to produce the desired product in the polymerization field in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Emulsion Polymerization Historical Review

Emulsion polymerization is a free radical initiated chain polymerization in which a monomer, or a mixture of monomers, is polymerized in an aqueous solution of a surfactant to form a product named as latex. Latex is defined as a colloidal dispersion of polymer particles in aqueous medium (Vineet, 2004). The polymer particles usually in spherical size, but they often have the morphology that will affects the end use properties deeply. The average size of the particles is from 0.05 to 5 nm in diameter. The latex produced in this process is a stable system. The charged particles cannot be recovered by ordinary separation procedures (Jr., 2007).

There are many models for emulsion polymerization in the literature. Table 2.1 lists the most comprehensive models presented in recent years (Gao & Penlidis, 2002).

Table 2.1 Models of emulsion homo-/copolymerization

Groups	Remarks	Systems
Alhamad et al.	comprehensive model (fixed pre-batch time for the seed formation in ab initio system)	Sty,MMA
Ballard	Copolymerization model for 0-1 systems	
Broadhead et al	Copolymerization model, CSTR operation, PSD , long chain branching frequency	Sty, BD
Congalidis et al	PSD, copolymerization model	MMA,sty
Coen et al.	PSD, particle number, particle size and amount of secondary nucleation	
Coen et al.	pseudo bulk kinetics included in the time evalution of particle size distribution	
Dougherty	Comprehensive model, MWD, PSD,	Sty/MMA
Dube et al.	copolymerization long-chain branching, copolymerization model, PSD, MWD	BD/AN
Forcada and Asua	Sequence length, PSD	Sty/MMA
Giannetti et al.	Reviews on PSD	
Giannetti	Copolymerization model	
Guillot	Thermodynamic aspects in copolymerization	Sty/AN
Hamielecd et.al.	Branching, crosslinking ,PSD,MWD	
Lichti et al.	Reviews on PSD, MWD	
Lin et al.	azeotropic composition, copolymerization model	Sty/AN
Mead and Poehlein	Copolymerizaiton model, PSD	Sty/MA,Sty/AN
Min and Ray	Comprehensive model, PSD, MWD	MMA
Nomura et al.	PSD,copolymerization model	MMA/sty
Penlidis et al.	CSTR reactor, PSD, MWD	PVC
Penlidis et al.	Batch reactor, PSD, MWD	VAc
Penlidis et al.	Dynamic and steady-state modeling of batch, semi-batch and CSTR reactor, PSD, MWD	
Penlidis et al.	comprehensive review, copolymerization model, PSD,MWD	PVC,VAc/PVC
Rawlings	Comprehensive model, PSD, MWD, CSTR stability	MMA, Sty, VAc
Richards et al.	An updated version of the early model of Congalidis et a., copolymerization model, no micellar nucleation assumed, MWD,PSD	MMA,MMA/Sty
Rawlings and Ray	An updated version of the early Min and Ray's model, PSD, MWD, CSTR operation, studies on CSTR oscillations	MMA
Saldivar et al.	Most recent version of Min and Ray's model, PSD, MWD, copolymerization model	MMA/Sty,Sty/α-methyl Sty,Sty/BD

Table 2.1 Continued

Storti et al.	Copolymerization model	AN/Sty/ MMA
Storti et al.	Modeling of molecular weight distribution	
Urretabizkaia et al.	Terpolymerization model	MMA/BA/VAc

The pioneer works for emulsion polymerization are done with comprehensive models, which couple kinetic models with reactor dynamics, for homo-and copolymerization. These models are presented by Liotta et al. (1998), Coen et al. (1998), Crowley et al. (2000), Gugliotta et al. (1995), Dougherty et al. (1986), Penlidis et al. (1986), Richards et al. (1989), Li and Brooks (1993), Zeaiter et al. (2002) and Alhamad et al. (2005).

Model for simulating the semibatch emulsion polymerization of styrene were developed by Li and Brooks (1993). In this model, the polymer seed particles were firstly time introduced in the reaction. The time evolution of the monomer conversion and the degree of polymerization over the whole course of the reaction were calculated in this model. Different monomer feed rates were used and a steady state in the reaction rate, under starved feed conditions, was obtained at low feed rates.

Coen et al. (1998) developed a kinetic model which incorporated all the complex competing events such as the aqueous phase propagation and termination, micellar nucleation, secondary nucleation, coagulation and diffusion, in a zero-one system. It is the recent advancement in the fundamentals of emulsion polymerization field. A detailed mechanistic dynamic model for styrene emulsion polymerization reactor was developed by Zeaiter et al. (2002). This model was used to predict the evolution of the polymer product MWD and PSD. A system with zero-one kinetics via free-radical mechanism steps was employed. The model comprised a set of rigorously developed population balance equations to predict the monomer conversion, PSD and MWD.

Alhamad et.al. (2005) has developed a comprehensive model for emulsion polymerization process of styrene and MMA using one fixed pre-batch time for the seed formation in *ab inito* system. The mass and energy balance in considered in the transient of the system. Population balance is used to describe the particle evolution in the development of model equations. The equations also incorporated the diffusion controlled kinetics at high monomer conversion where the transient of regime from “zero one” to “pseudo-bulk” occurs. In *ab initio* emulsion polymerization, pre-batch time is needed for the seed formation and to eliminate any dissolved oxygen from the system. (Wan Ibrahim, 2011)

By using accurate kinetic models, the relationship between process variables and the product characteristics that they influence can be observe in the process easily. At the same time, their purpose can be manifold easily from time to time. It can be concluded that by using accurate kinetic modeling, time can the save. By using the software to build the model, the number of experiments can be reduced. Consequently, cost and effort in order to investigate the effects of changes can be saving too.

The end use properties of polymers are depends on the specific molecular weight averages. As a result, molecular weight is very important. Thus, maximizing overall conversion (X_n) is very important factor to reduce the downstream separation as well as decrease the operation cost. Alhamad et al.(2005) and Wan Ibrahim (2011) both have considered maximization of M_n for emulsion polymerization of styrene and MMA for a given total amount of monomer fed to the reactor.Wan Ibrahim (2011) also considered the X_n in her work. Her result approved that decrease of pre-batch time will increase the M_n and the desired molecular weight can be achieved in shorter time. Consequently, it can increase the overall conversion. (Wan Ibrahim, 2011)

In this work, the model of Alhamad (2005) will be used for the dynamic optimization for emulsion polymerization of styrene and MMA in batch reactor. The dynamic problem with the objective function to maximize overall conversion (X_n) is considered. The X_n will be maximized for a given M_n by optimizing initiator flow rates(F_I), surfactant flow rates (F_s) and reactor jacket temperature(T_{jo}).

2.2 Properties of Styrene

Styrene is an organic compound with the chemical formula $C_6H_5CH=CH_2$. It appears as a colorless oily liquid that evaporates easily and has a sweet smell, although high concentrations confer a less pleasant odor. Styrene monomer is a basic building block of the plastic industry. It is used to make a host of downstream derivative products that go into millions of consumer goods. Primary derivatives of styrene monomer are included polystyrene, expandable polystyrene (EPS) and acrylonitrilebutadiene-styrene (ABS)/styrene-acrylonitrile (SAN) resins, styrene butadiene (SB) latex, SB Rubber (SBR), unsaturated polyester resins (UPR), specialty polymers, co-polymers and styrene thermoplastic elastomers (TPE)(2004).

Table 2.2 Physical Properties of Styrene Monomer

Properties	
Physical State	Liquid
Color	Colorless
Molecular Weight	104.152
Boiling Point	145.2^{o}C
Freezing Point	-30.6^{o}C
Density at 25^{o}C	0.9011 g/ml
Vapor Pressure at20^{o}C	5 mmHg
Coefficient of Cubical Expansion at 20^{o}C	0.000971^{o}C^{-1}
Critical Temperature	363^{o}C
Critical Pressure	3.84MPa 557.0psia
Critical Volume	3.38 cc/g 0.0541 ft^{3}/lb
Heat/Combustion,Liquid@25^{o}C	-1019Kcal/mol
Heat/Formation, Vapor@25^{o}C	35.23 Kcal/mol
Heat Formation, Liquid@25^{o}C	24.84 Kcal/mol
Flash Point	31.9^{o}C
Solubility at 20^{o}C	water: 0.032 wt% Alcohol:∞ Ether: ∞
saturated concentration in air at 25^{o}C	0.81 mol% 2.84 wt%
Heat/ Polymerization at 25^{o}C	16.68 Kcal/mol

(Sources: LYONDELL,(2004))

2.3 Properties of Methyl Methacrylate (MMA)

Methyl methacrylate (MMA) is an organic compound with the formula $CH_2{=}C(CH_3)COOCH_3$. It appears as a colorless, volatile liquid with an acrid fruity odor. The purity of commercial MMA is typically 99.9%. It contains traces of acidity as methacrylic acid (0.003% max.; specification, 0.005% max.) and water

(0.03% max.; specification, 0.05% max.). Inhibitors added for storage and transportation are usually 2–100ppm methyl ether of hydroquinone and 25–100 ppm hydroquinone, although other phenolic inhibitors, such as dimethyl tert-butylphenol, may also be used (Ms W.Dormer, 1998).

It readily polymerizes on exposure to light, heat, oxygen, ionizing radiation, or catalysts. It is used primarily to make a variety of resins and plastics, and is most often polymerized to polymethyl methacrylate, which is used to make acrylic sheets, acrylic moldings, and extrusion powders. MMA is also copolymerized with other acrylates and used to make surface coating resins, lacquers, and emulsion polymers. The chemical is used in medicine and dentistry to make prosthetic devices and as a ceramic filler or cement.

Table 2.3 Physical Properties of Methyl Methacrylate (MMA)

Properties	
Physical State	Liquid
Color	Colorless
Molecular weight	100.11
Density	0.94 g/cm^3
Vapor Density(air = 1)	3.45
Vapor Pressure at 20oC	29.33 mmHg
Melting Point	-48^{o}C
Boiling Point	100-101 ^{o}C
Viscosity at 20^{o}C	0.6cP
Flash point	2^{o}C
Specific gravity at 20^{o}C	0.945
Heat of polymerization	-138 cal/g
Vapor Pressure at 25^{o}C	40 mmHg
Solubility	• Slightly soluble in water • soluble in alcohol, ether, aceone, methyl ethyl ketone, tetrahydrofuran, hydrofuran, ester, aromatic and chlorinated hydrocarbons

(Source: (EPA)

2.4 Properties of Persulfate

Persulfate are ions or compounds with more oxygen than normal sulfates. They do not have sulfur in a different oxidation state but they contain peroxide units, where two oxygens take the place of one in a normal sulfate; the oxygen atoms are in oxidation state −1(as shown in Figure 2.1) . Persulfate is one of the common oxidizing agent used for in-situ chemical oxidation applications.. Usually it applied in the subsurface as sodium persulfate ($Na_2S_2O_8$), potassium persulfate ($K_2S_2O_8$) and ammonium persulfate $(NH_4)_2S_2O_8$

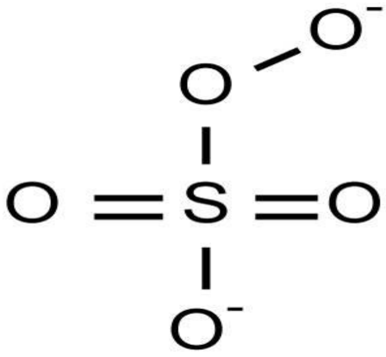

Figure 2.1 Persulfate Chemical Structure

In this study, potassium persulfate is chosen as the initiator. In chemical industries, it used for non-chlorine oxidation. It may apply in many industries. For instance, printed circuit board etching, activation of copper and aluminum surfaces, polymerization initiator, modification of starch, paper and textile cold bleaching and others. Table 2.4 showed the physical-chemical properties of Potassium persulfate.

Table 2.4 Physical Properties of Potassium Persulfate

Properties	
Molecular formula	$K_2S_2O_8$
Molar mass	270.322 g/mol
Appearance	white powder
Odor	odorless
Density	2.477 g/cm^3
pH	5-8 for 1% solution
Melting point	<100oC decomposes
Solubility in water	1.75 g/100mL (0^{o}C) 5.29 g/100mL (20^{o}C)
Solubility	insoluble in alcohol
Refractive Index (nD)	1.467

(Sources: SIDS, O. (2005)1)

2.5 Properties of Sodium Decoeyl Sulfate (SDS)

Sodium Decoeyl Sulfate (SDS or NaDS) is an organic compound with the formula $CH_3(CH_2)_{11}OSO_3Na$. It usually used as an anionic surfactant used in many cleaning and hygiene products. The salt is of an organosulfate consisting of a 12-carbon tail attached to a sulfate group, giving the material the amphiphilic properties required of a detergent. Being derived from inexpensive coconut and palm oils, it is a common component of many domestic cleaning products.

Table 2.5: Physical Properties of Sodium Decoeyl Sulfate (SDS)

Properties	
Molecular formula	$NaC_{12}H_{25}SO_4$
Molar Mass	288.372 g/mol
Appearance	white or cream-colored solid
Odor	odorless
Density	1.01 g/cm^3
Melting Point	206^{o}C
Refractive index (n_D)	1.461

(Source: (Marrakchi S, 2006)

2.6 Description of the Emulsion Process

As relatively stable macro-radicals are produced in the emulsion polymerization, the termination rate decreases and a high molecular weight product is rapidly produced. The ingredients for an emulsion polymerization are included a water soluble initiator, a chemical emulsifier/surfactants, and a monomer that is only slightly soluble in water or completely insoluble. It is customary to use a water soluble initiator such as potassium persulfate and an anionic surfactant such as sodium stearate, and to stir the aqueous mixture of monomer, initiator, and surfactant in the absence of oxygen at 40^{o}C to 70^{o}C(Jr., 2007)

The emulsion polymerization starts in the aqueous phase. The monomers are dispersed in water in the presence of surfactants. The surfactants adsorb on the surface of the monomer droplets. Surfactants serve the purpose of lowering the surface tension at monomer-water interphase and facilitate emulsification of the monomer in water. Ionic surfactant will stabilize the droplets by electrostatic repulsion while non-ionic surfactants provide steric stabilization. In most formulations, the amount of surfactant exceeds that needed to completely cover the monomer droplets and saturate the aqueous phase. Other surfactants form small aggregates called micelles that are swollen with monomer.

Initiators used in the process is carried out at elevated temperature (75-90 ^{o}C), and redox system is used to lower the temperatures when a high rate of initiation is carried out. Since most of the initiators are water-soluble, therefore the primary radicals are formed in aqueous phases. These radicals are cannot directly enter into the organic phase because they are too hydrophilic. Therefore, they react with the monomer dissolved in the aqueous phase, forming oligoradicals which play an important role in nucleation as per the existing (heterogeneous and homogeneous coagulative and droplet) nucleation theories. These oligoradicals will grow slowly because of the low concentration of monomer in the aqueous phase. The oligoradicals become hydrophobic enough to be able to enter into organic phases of the system after adding some monomer units. The entering oligoradicals find monomer-rich environment within the micelles, and hence they grow fast forming a polymer chain. A polymer particle is formed when the new species formed upon entry of a radical into a micelle. This process is called heterogeneous nucleation. When the oligoradicals grow in the aqueous phase beyond the length at which they are still soluble in water and precipitate, the polymer particle may form. The emulsifier in the aqueous phase may stabilize the precipitated polymer chain while monomer diffuses into the new organic phase will allow a fast growth for the polymer chain. This process of formation of polymer particles by precipitation of oligoradicals is named as homogeneous nucleation (Maria J.Barandiaran, 2007)

Three stages will be go though by emulsion polymerization. In the first stage, polymer particles are generated as per the heterogeneous nucleation mechanism. The particles grow in size as the reaction progresses inside them. The monomer droplets serve as the supply reservoirs of the monomer to the particles in which the reaction is talking place. Polymer particles continue to grow in second stage by absorbing more monomer from the monomer droplets, which serve as a monomer reservoir. The second stage is thus characterized by the growth of the polymer particles and decreasing size of monomer droplets. At the end of the first stage, the monomer conversion is about 5-10% typically. The second interval ends when all monomer droplets are consumed. The monomer conversion at which second stage ends depends on the extent in which the polymer particles are swollen by the monomer. On the basis of thermodynamic equilibrium, the monomer concentration in the polymer particles during the first and second intervals remains relatively constant. In the third interval, polymerization is completed when all the monomer all the monomer left in the particles is consumed or a limiting conversion is reached (Gao & Penlidis, 2002).

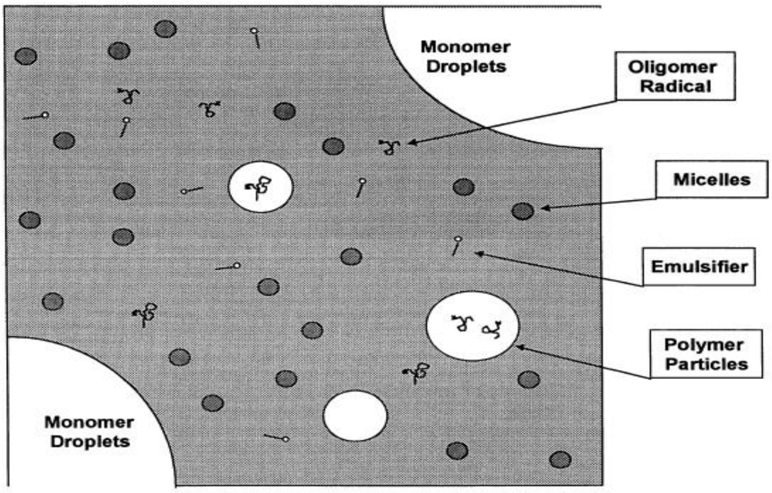

Figure 2.2: Emulsion Polymerization Diagram (stages I and II)

2.7 Kinetic Mechanisms

Figure 2.3 display the most important phenomena in a typical emulsion reaction. In emulsion polymerization most of the polymerization occurs in the polymer particles. Radicals formed in the aqueous phase from water-soluble initiators, react with the monomer dissolved in the aqueous phase forming oligoradicals. These oligoradicals may

(1) Enter into the polymer particles

(2) Enter into the micelles (heterogeneous nucleation),

(3) Propagate in the aqueous phase until they become insoluble and precipitate forming new polymer particles (homogeneous nucleation) and

(4) Terminate with other radicals in the aqueous phase.

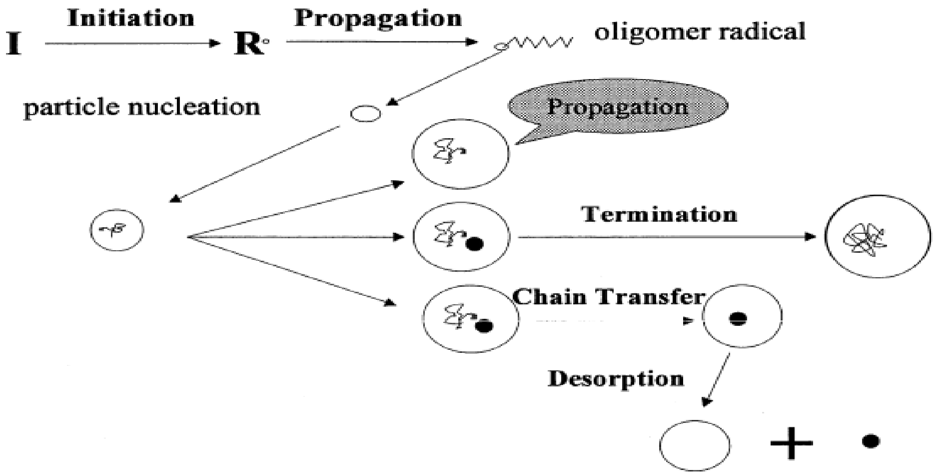

Figure 2.3 Emulsion Polymerization Diagram

The likehood of each of these events depends on the particular conditions of the system, for example the number of polymer particles, emulsifier concentration, initiator concentration, monomer type and concentration(Maria J.Barandiaran, 2007).

2.8 Advantages and Disadvantages of Emulsion Process

The advantages of emulsion polymerization are

(1) Ease of control, the viscosity of the reaction mass is much less than that of a true solution of a comparable concentration, the water acts as its heat capacity and the reaction mass may be refluxed.

(2) It is possible to obtain both high rates of polymerization and high average chain length through the use of high surfactant soap and low initiator concentration.

(3) The latex produced is often directly valuable.

The disadvantages of emulsion polymerization are

(1) It is difficult to get polymer. The tremendous surfaces are of the tiny particles providing plenty of rooms for absorbed impurities.

(2) Considerable technology is required to recover the solid polymer.

(3) The water in the reaction mass lowers the yield per reaction.

2.9 gPROMS Software

gPROMS stands for a general PROcess Modeling System. This software is edited by Process Systems Enterprise. Its proven capabilities for the simulation, optimization and parameter estimation (both steady-state and dynamic) of highly complex processes make it become the leading Advanced Process Modeling for the process industries. It is used to apply across application areas in all process sectors. Its process modeling, process simulation and optimization capabilities are used to generate high accuracy predictive information for decision support in product and process innovation, design and operation.

2.9.1 gPROMS advantages

2.9.1.1 Clear, concise language

gPROMS provide a platform by using equation-oriented approach. The users can use the equation on the paper into the model builder directly without any alteration. Users have no worry to the complexity of the solution techniques.

2.9.1.2 Modeling of process discontinuities

It’s normal for a process if there is the discontinuous of physical and chemical behavior. It may cause by the phase transitions, flow regime transition, geometrical limitations and so on. Many commercial simulators have no capability to solve this problem but gPROMS can handle this problem. Reversible-symmetric, reversible-asymmetric and irreversible discontinuities can all be routinely handled. The algorithms within gPROMS were developed to detect the discontinuities automatically and lock on to them and then re-initialize rapidly.

2.9.1.3 Modeling of operating procedures

The operating procedures are same important as the physical or chemical properties in the unit operations. All the equations can solve in a model only but not need to solve in multiple models like other commercial simulators. From the view of gPROMS, the processes are combination of equipment models and their operating procedures. It adopts a dual description for processes in terms of MODELs and TASKs. This features is quite important, especially for the batch processes where the description of operations is only half of the story while another half being the description of the operating policy that is used to run the plant.

2.9.4 Dynamic Optimization

gPROMS was the first modeling system to have formal, mathematical algorithms for automatically optimizing large-scale, dynamic processes (both lumped and distributed). Its optimization capabilities include talking into account integer or discrete decisions using Mixed Integer Optimization (MIO). MIO can be applied to both steady-state and dynamic gPROMS models. The discontinuous equations such as IF and CASE equations can be involved in the gPROMS environment. In addition, this software can optimize for the systems which is involving 40000 time-varying quantities in the same time. For instance, the system involved the optimal start-up and shut-up procedures, optimal design and operation of multi-phase batch/semibatch reactors as well as optimal tuning of PID controllers.

2.9.1.5 Parameter estimation

gProms have a special feature. Estimating model parameters through optimization from both steady-state and dynamic experimental data is allowed in the system. By using this ability, it lets the users to complete the flexibility in that they can specify different variance models for different variables in different experiment. Besides, the build-in interface to MS Excel will make the users easier to have another testing for statistical analysis of the results, generate plots overlaying model data and experimental data, plot confidence ellipsoids as well.

CHAPTER 3

KINETIC AND DYNAMIC MODELING

The main objective of modeling emulsion polymerization processes is to gain fundamental understanding of the dynamic behavior of the system in order to optimize and control the process for desired product characteristics.

Emulsion polymers are produced by process, meaning that the manner in which the polymerization is carried out is more important than the raw materials in determining the form of the final product properties. Emulsion polymerization is a sensitive process. It must be handle carefully during manufacturing process to ensure the consistency of the final product from batch to batch. Therefore, the way to control the emulsion polymerization process is essential.

The heterogeneous nature of emulsion homo-polymerization and the numerous mechanisms I involved in the system cause complications in the understanding of the kinetics involved.

A set of assumptions is set to construct the model. These assumptions included:

1. The process starts with a zero-one system and later shifts to pseudo-bulk system at high conversion in which diffusion-controlled kinetics mediate this transition.

2. The concentration of the three monomers in the different phases are in thermodynamic equilibrium.

3. Pseudo-steady state assumption for radicals in the aqueous and polymer particles phase apply.

4. The kinetic equations are based on the terminal model.

5. There is no particle coagulation. All surfactants are used in process to stabilize the system.

6. Three types of particles are identified in the system. They are particles containing no radicals (n_o), particles containing one monomeric radical(n_1^m) and particles containing one polymeric radical(n_1^P).

7. Particle size is monodisperse. If particles are generated in stage I in a relatively short period of time, this assumption holds.

8. Reactor is perfectly mixed.

9. The main loci of polymerization are the polymer particles.(Gao & Penlidis, 2002)

The equations of emulsion polymerization are developed in this work based on the fundamentals of kinetics and thermodynamics equilibrium. The dynamic optimizations for emulsion polymerization of Styrene and MMA in batch reactor are carried out using a commercial package, gPROMS software. In the model, Control Vector Parameterization (CVP) technique has been applied. This converts the dynamic optimization problem into a Nonlinear Programming (NLP) problem which is solved by standard SQP method available in gPROMS software.

3.1 Radical Balances in the Aqueous Phase

Based on (Wan Ibrahim, 2011) and (Alhamad, Romagnoli, & Gomes, 2005), a system with zero-one for emulsion copolymerization of styrene and MMA is taken. The process begins with the decomposition of initiator (I) molecule to form free radicals in aqueous phase which then propagate with the monomers A and B to generate oligomeric radicals.

$I - I \xrightarrow{k_d} 2I^{\cdot}$ (Reaction1)

$I^{\cdot} + M \xrightarrow{k_{p1}} IM_1^{\cdot}$ (Reaction2)

where $k_d$is the rate constant for initiator decomposition(s^{-1}) and k_{p1} is the propagation coefficient(1/ mol s) .

The primary radical will undergo propagation process by propagating with monomer A (styrene) or B (MMA) which $k_{p,A}$ and $k_{p,B}$ are coefficient of monomer A and B.

$I^{\cdot} + M_A \xrightarrow{k_{p,A}} IM_A^{\cdot}$ (Reaction3)

$I^{\cdot} + M_B \xrightarrow{k_{p,B}} IM_B^{\cdot}$ (Reaction4)

Then these oligomeric radicals formed could be will $IM_A^{\cdot}$ or $IM_B^{\cdot}$.They will undergo a sequence of reactions as following:

$IM_1^{\cdot} + M \xrightarrow{k^i{}_{p,aq}} IM_{i+1}^{\cdot}$ (Reaction5)

These oligomeric radicals will continue the propagation process with monomer A or monomer B with coefficient of $k_{p,AA}, k_{p,AB}, k_{p,BB}, k_{p,BA}$.

$IM_A^{\cdot} + M_A \xrightarrow{k_{p,AA}} IM_{AA}^{\cdot}$ (Reaction6)

$$IM_A^{\cdot} + M_B \xrightarrow{k_{p,AB}} IM_{AB}^{\cdot} \qquad \text{(Reaction7)}$$

$$IM_B^{\cdot} + M_A \xrightarrow{k_{p,BA}} IM_{BA}^{\cdot} \qquad \text{(Reaction8)}$$

$$IM_B^{\cdot} + M_B \xrightarrow{k_{p,AA}} IM_{BB}^{\cdot} \qquad \text{(Reaction9)}$$

Four different types of radical species will be addressed and balanced in the aqueous phase. There are the oligomeric radicals of degree 1; oligomeric radicals for degree greater than 1 and less than z; oligomeric radicals degree greater than or equal to z and less than $j_{crit} - 1$, and oligomeric when it achieved the j_{crit}. The balance equation for oligomeric mentioned above can be represented by the equation below:

$$IM_1 = \frac{2k_d[I]}{k_{p,aq}^{1} C_w + k_{t,aq} T} \qquad (1)$$

$$IM_i = \frac{k_{p,aq}^{i-1} IM_{i-1} C_w}{k_{p,aq}^{i} C_w + k_{t,aq} T} \quad for\ i = 2\ to\ (z-1) \qquad (2)$$

$$IM_i = \frac{k_{p,aq}^{i-1} IM_{i-1} C_w}{k_{p,aq}^{i} C_w + \sum(k_e^i n)\Delta r + k_{e,micelle}^{i} C_{micelle} + k_{t,aq} T} \quad for\ i = z\ to\ (j_{crit} - 1) \qquad (3)$$

$$IM_{jcrit} = \frac{k_{p,aq}^{jcrit-1} IM_{jcrit-1} C_w}{k_{t,aq} T} \qquad (4)$$

In these equations, C_w the monomer concentration in the water phase and T is total concentration of the radicals in the aqueous phase.

Transfer events between polymeric radical and monomeric radical, $M^{\cdot}$ may occur. This process is a reversible process as shown in Reaction 10.

$$E^{\cdot} + particle \underset{k_d M}{\overset{\mathrm{k_eE}}{\longleftrightarrow}} (particle - M^{\cdot}) \qquad \text{(Reaction10)}$$

$$E = \frac{\sum_1^G (k_{dm}^{j} n_{1,m}^{j})\Delta r}{k_{eE}^{1} C_{micelle} + \sum_1^G (k_{eE}^{j} n^{j})\Delta r + k_{t,aq} T} \qquad (5)$$

T is the total radical concentration in the aqueous phase. It is given by:

$$T = \sum IM + E \qquad (6)$$

3.2 Particle Population Balance

Three different types of particles are classified in the zero-one system, n_o, n_1^p and n_1^m .This distinction is necessary because polymeric and monomeric radicals undergo different kinetic events. The total population of particles (n) is given by:

$$n = n_o + n_1^m + n_1^p \tag{7}$$

Based on the assumption mentions as previous, the time evolution equations of particle size distribution are given as below:

$$\frac{\partial n_1^p(V,t)}{\partial t} = \frac{\partial (V-V_o)}{\Delta r}(k_{p,aq}^{jcrit-1} C_w IM_{jcrit-1} + \sum_1^{jcrit-1} k_{e,micelle} C_{micelle} IM_i) +$$

$$k_p C_p n_1^m + p_{init} n_1^o - p n_1^p - k_{tr} C_p n_1^p - \frac{\partial (K n_1^p)}{\partial V} + \int_o^\infty B(V, V-V')\left[n_o(V') n_1^p(V -\right.$$

$$V'+n1pV'noV-V'dV'-n1p0\infty BV-V'[noV'+n1p(V')]dV' \tag{8}$$

$$\frac{\partial (K n_{1,1}^p)}{\partial V} = \frac{K}{8\pi \Delta r} \frac{n_{1,2}^p}{(r_{uns,2})^2} \tag{9}$$

$$\frac{\partial n_1^m(V,t)}{\partial t} = k_{tr} C_p n_1^p + k_{eE}[E] n_o - (k_p C_p + p + k_{dm}) n_1^m \tag{10}$$

$$\frac{\partial n_o(V,t)}{\partial t} = p(n_1^p + n_1^m - n_o) + k_{dm} n_1^m + \int_o^\infty B(V, V-V')[\,n_o(V') n_o(V-V') +$$

$$n_1^p(V') n_1^p(V-V')]dV' - n_o(V) \int_o^\infty B(V, V')[\,n_o(V') + n_1^p(V')]dV' \tag{11}$$

The area of particle is given as

$$Area_{particle} = (36\pi x N_{tot})^{1/3} x {V_p}^{2/3} \tag{12}$$

The average diameter and radius of the particles are estimated as follows:

$$Diameter_{particle} = (\frac{Area_{particle}}{\pi N_{tot}})^{1/2} \tag{13}$$

$$Radius_{particle} = \frac{\sum (r_{uns} n)}{\sum n} \tag{14}$$

The particle size polydispersity index, PSPI is given by the mean squared radius divided by the mean radius squared

$$PSPI = \frac{<r^2>}{<r>^2} \tag{15}$$

Where the mean squared radius is

$$< r^2 \geq \frac{\sum_{i=1}^{G} n(i)r(i)^2}{\sum_{i-1}^{G} n(i)} \tag{16}$$

3.3 Molecular Weight Distribution

It is important to evaluate the polymer properties, molecular weight distribution (MWD) instead of the average molecular weight because a polymer sample consists of a large number of individual chains and these individual chains have different average molecular weight. The molecular weight distribution are linked to the polymer structure and can be described in terms of average molecular characteristics., such as number average molecular weight (M_n), weight average molecular weight (M_w), and molecular weight polydispersity index (MWPI). Mn and Mw are defined as the average number and weight of dead, non-growing, chains with a given molecular weight respectively which are expressed by:

$$M_w = \frac{\sum M^2 P(M)}{\sum MP(M)} \tag{17}$$

$$M_n = \frac{\sum MP(M)}{\sum P(M)} \tag{18}$$

The molecular weight polydispersity index is given by:

$$MWPI = \frac{M_w}{M_n} \tag{19}$$

Although the molecular weight distribution may be governed by the kinetics affecting the rate, it is determined entirely by the chain-stopping and chain-growth events. Assumption is made to assume that the transfer of radical events occurs only to monomers and chain-transfer agents, while there is no polymer transfer. Gilbert (1995) put a simplified equation for instantaneous molecular weight distribution with the absence of chain-transfer agent.

$$\frac{\partial \bar{P}(M)}{\partial t} = P(M) = (k_{tr}C_p + p_{avg})\bar{n}\exp\left(\frac{-(p + k_{tr}C_p)}{k_p C_p}\frac{M}{M_w}\right) \tag{20}$$

Where M is the molecular weight of the polymer chain, P(M) is the instantaneous MWD, and $\bar{P}(M)$is the cumulative MWD.

3.4 Rates of Polymerization Reactions

The polymerization reactions occur in the particle and aqueous phases but not in the droplet phase. The instantaneous rate of polymerization for monomer A and B are calculated by the following equations:

$$R_{pAp} = \frac{\left(k_{pAA}K_{pBB}\left(r_A C_{pA}^2 + C_{pA}C_{pB}\right)\right)}{k_{pBB}r_A C_{pA} + k_{pAA}r_B C_{pB}} . \frac{\bar{n}N_{tot}}{N_a V_p} \tag{21}$$

$$R_{pBp} = \frac{\left(k_{pAA}K_{pBB}\left(r_B C_{pB}^2 + C_{pA}C_{pB}\right)\right)}{k_{pBB}r_A C_{pA} + k_{pAA}r_B C_{pB}} . \frac{\bar{n}N_{tot}}{N_a V_p} \tag{22}$$

$$R_{pAw} = \frac{\left(k_{pAA}K_{pBB}\left(r_A C_{wA}^2 + C_{wA}C_{wB}\right)\right)}{k_{pBB}r_A C_{wA} + k_{pAA}r_B C_{wB}} . T \tag{23}$$

$$R_{pBw} = \frac{\left(k_{pAA}K_{pBB}\left(r_B C_{wB}^2 + C_{wA}C_{wB}\right)\right)}{k_{pBB}r_A C_{wA} + k_{pAA}r_B C_{wB}} . T \tag{24}$$

3.5 Reactor Material Balance

The material balances for the initiator (I), emulsifier (S), and water (Vwo) are:

$$\frac{d[I]}{dt} = -2k_d f[I] + \frac{F_I}{V_w} \tag{25}$$

$$\frac{dS}{dt} = \frac{F_s}{V_w} \tag{26}$$

$$\frac{dV_{wo}}{dt} = F_w \tag{27}$$

The material balance for monomers A and B are as follows:

$$\frac{dN_{m,A}}{dt} = F_{mA,in} - R_{pAp}V_p - R_{pAw}V_w \tag{28}$$

$$\frac{dN_{m,B}}{dt} = F_{mB,in} - R_{pBp}V_p - R_{pBw}V_w \tag{29}$$

$$\frac{dN_{pol,A}}{dt} = R_{pAp}V_p + R_{pAw}V_w \tag{30}$$

$$\frac{dN_{pol,B}}{dt} = R_{pBp}V_p + R_{pBw}V_w \tag{31}$$

Where $N_{pol,A}$and $N_{pol,B}$are the number of moles of copolymer having its terminals as A and B, respectively.

The number of moles of monomer fed to the reactor is calculated by:

$$\frac{dN_{m,A}^{fed}}{dt} = F_{mA,in} \tag{32}$$

$$\frac{dN_{m,B}^{fed}}{dt} = F_{mB,in} \tag{33}$$

Where $F_{mA,in}$and $F_{mB,in}$are the molar flow rates of monomer A and B, respectively.

3.6 Physical Parameters

3.6.1 Monomer Concentrations in Multiple Phases

Emulsion polymerization process can be divided into three types of phases: the water or aqueous phase (w), the particle phase (p), and the droplet phase (d). The partitions of the monomers among the three phases undergo thermodynamic equilibrium, consequently it is same for the partial molar free energies of monomer in the different phase.

$$\left(\frac{\Delta G}{R.T}\right)^{p} = \left(\frac{\Delta G}{R.T}\right)^{w} = \left(\frac{\Delta G}{R.T}\right)^{d} \tag{34}$$

The partition coefficients (K) between each of the two phases are derived from the thermodynamic equilibrium condition at the saturation state (Hamielec et al.,1987):

$$K_{A,wp} = \frac{C_{w,A}^{sat}}{C_{p,A}^{sat}} \tag{35}$$

$$K_{A,mp} = \frac{d_{m,A} K_{A,wp}}{M_{w,A} C_{w,A}^{sat}} \tag{36}$$

$$K_{B,wp} = \frac{C_{w,B}^{sat}}{C_{p,B}^{sat}} \tag{37}$$

$$K_{B,mp} = \frac{d_{m,B} K_{B,wp}}{M_{w,B} C_{w,B}^{sat}} \tag{38}$$

$$K_{A,mw} = \frac{K_{A,mp}}{K_{A,wp}} \tag{39}$$

$$K_{B,mw} = \frac{K_{B,mp}}{K_{B,wp}} \tag{40}$$

where $d_{m,B}$ is the density of monomer B and $M_{w,B}$ is the molecular weight of monomer B, and $C_{w,B}^{sat}$ is the saturated concentration of monomer B in the water phase.

The concentration of monomers in particle phase can attain a maximum of the saturated value during the intervals I and II of the emulsion polymerization. Its value usually decreases in interval III due to the absence of monomer droplets in this interval. The concentration of styrene and MMA in the particle phase is calculated as follows:

$$C_p = P_A C_{p,A} + P_B C_{p,B} \tag{41}$$

Where $C_{p,A}$ and $C_{p,B}$ are the concentrations of monomers A and B in the particle phase.

The concentrations in the water phase are calculated using the partition coefficients between the three different phases. $C_{p,A}$ and $C_{p,B}$ may reach a maximum value of saturated monomer concentrations in the particle phase and are calculated as follows:

$$C_{p,A} = MIN(C_{p,A}^{sat}, \frac{N_{m,A}}{K_{A,mw}K_{A,wp}V_m + K_{A,mp}V_w + V_p}) \tag{42}$$

$$C_{p,B} = MIN(C_{p,B}^{sat}, \frac{N_{m,B}}{K_{B,mw}K_{B,wp}V_m + K_{B,mp}V_w + V_p}) \tag{43}$$

$$C_{w,A} = MIN(C_{w,A}^{sat}, C_{p,A}K_{A,wp}) \tag{44}$$

$$C_{w,B} = MIN(C_{w,B}^{sat}, C_{p,B}K_{B,wp}) \tag{45}$$

$$C_w = f_A C_{w,A} + f_B C_{w,B} \tag{46}$$

Where $C_{p,A} and\ C_{p,B}$ are the saturated concentrations of A and B in the particle phase, respectively;

3.6.2 Volumes of Phases

The volumes of the monomer, water and organic phase are represented by V_m, V_w and V_{org} each. The following equation used to find water phase volume as below:

$$V_w = \frac{V_{wo}}{1-(M_{w,A}/C_{w,A})-(M_{w,B}/C_{w,B})} \tag{47}$$

While the volume of the monomer phase is given as follows:

$$V_m = \frac{N_{m,avg}M_w}{d_{avg}} \tag{48}$$

$N_{m,avg}$ is the average number of moles given as

$$N_{m,avg} = f_A N_{m,A} + f_B N_{m,B} \tag{49}$$

and d_{avg} is the average density of the monomers styrene and MMA.

$$\frac{dV_{org}}{dt} = \frac{F_{mA,in}M_{w,A}}{d_{m,A}} + \frac{F_{mB,in}M_{w,B}}{d_{m,B}} - shrinkage \tag{50}$$

$$\text{Shrinkage}=\sum_{i=A}^{B}\left\{M_i\left(R_{pip}V_p + R_{piw}V_w\right)\left(\frac{1}{d_{m,i}} - \frac{1}{d_{p,i}}\right)\right\} \tag{51}$$

The volume of polymer particles, V_p is defined for two separate regimes: when monomer droplets exist and when monomer droplets cease to exit. Thus, two different equations are used to calculate the copolymer particle volume in two stages. For the first stage the conversion is about 40%, while when interval II ends and interval III begins, the concentration of monomer droplets starts to decrease. The V_p for first regime is calculated by

$$\frac{dV_p}{dt} = \frac{M_{w,A}\left(R_{p,A,p}V_p+R_{p,A,w}V_w\right)+M_{w,B}\left(R_{p,B,p}V_p+R_{p,B,p}V_w\right)}{d_p} \tag{52}$$

Whereas for second regime, V_p is given by

$$\frac{dV_p}{dt} = \frac{M_{w,A}\left(R_{p,A,p}V_p + R_{p,A,w}V_w\right) + M_{w,B}\left(R_{p,B,p}V_p + R_{p,B,p}V_w\right)}{d_p} - \left[M_{w,A}R_{p,A,p}V_p\left(\frac{1}{d_{m,A}} - \frac{1}{d_{p,A}}\right) + \right.$$

$$Mw,BRp,B,pVp1dm,B-1dp,B \tag{53}$$

The volume of the monomer can be calculated by the difference between the volume of the organic phase and the sum of the volumes of polymer particles and of monomer in the aqueous phase.

3.6.3 Swollen Radius of a Particle

The relationship between swollen radius, r_s, and unswollen radius, r_{uns}, of a particle are as follows:

$$r_s^j = r_{uns}^j x \left(\frac{d_{avg}}{d_{avg} - C_p M_w}\right)^{1/3} \tag{54}$$

3.6.4 Concentration of Micelles

Two types of nucleation are occurred for particle formation in emulsion system. They are micellar nucleation and homogeneous nucleation; Micellar nucleation is the major source for particle formation because it is used to predict the concentration of micelles in the aqueous phase in this system. Usually, the concentration of surfactant in the aqueous phase is distributed into two parts. One part is adsorbed onto the particle surface and another part is dissolved in the aqueous phase. If there is excess of surfactant added into the system, then the remaining amount will contribute to the formation of micelles. Therefore concentration of micelle is given as follows

$$C_{micelle} = Max\left[0, \frac{[S_{added}]-[S_{ads}]-[cmc]}{n_{agg}}\right] \tag{55}$$

$$S_{ads} = \frac{4\pi\sum_{i=1}^{G}(r_{s,i}^{2}n_i)}{a_s} \tag{56}$$

where [S_{added}] is the total concentration of surfactant; a_s is the area occupied by an adsorbed surfactant molecule; n_{agg} is the average number of surfactant molecules in a micelle and [CMC] is the critical micelle concentration. When the surfactant concentration falls below the CMC, the formation via micelles will stops.

3.6.5 Critical Degrees of Polymerization

Homogenous nucleation occurs when an oligomeric radical is no longer soluble in the aqueous phase (Priest, 1952). The oligomeric radicals start to collapse when it attains a critical degree of polymerization, jcrit. The critical degree for homogeneous nucleation is given as follows:

$$j_{crit} = 1 + \frac{-55(KJ.mol^{-1})}{R.T.InC_{w}^{sat}} \tag{57}$$

Micellar nucleation occurs when an oligomeric radical enters a micelle and a particle forms. For the entry of oligomeric radical into a micelle, it must have propagated to a critical degree, z. The critical degree for micellar nucleation is given as follow:

$$z = 1 + \frac{-23(KJ.mol^{-1})}{R.T.InC_{w}^{sat}} \tag{58}$$

3.6.6 Probability Functions

The probability of the reactions of radicals in the water phase, $\emptyset_A and\ \emptyset_B$are defined as follows:

$$\emptyset_A = \frac{k_{pBA}f_A}{k_{pBA}f_A + k_{pAB}f_B} \tag{59}$$

$$\emptyset_B = 1 - \emptyset_A \tag{60}$$

The propagational probabilities in the water phase, F_1 and F_2 are given as:

$$F_1 = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2} \tag{61}$$

$$F_1 = 1 - F_2 \tag{62}$$

The probability of a monomeric radical of type I reacts in the aqueous phase by either propagation or termination is given by

$$\beta_A(j) = \frac{k_{pAA}C_{w,A} + k_{pAB}C_{wB} + (k_{tAA}P_A + k_{tAB}P_B)T}{k_{pAA}C_{w,A} + k_{pAB}C_{wB} + (k_{tAA}P_A + k_{tAB}P_B)T + \sum k_e(j) N_{tot} \emptyset_B / N_a + \sum k_{e,micelle}} \tag{63}$$

$$\beta_B(j) = \frac{k_{pBA}C_{w,A} + k_{pBB}C_{wB} + (k_{tBA}P_A + k_{tBB}P_B)T}{k_{pBA}C_{w,A} + k_{pBB}C_{wB} + (k_{tBA}P_A + k_{tBB}P_B)T + \sum k_e(j) N_{tot} \emptyset_B / N_a + \sum k_{e,micelle}} \tag{64}$$

3.7 Rate Coefficients

In a emulsion homopolymerization system, it is comprised of many complicated kinetic coefficients and parameters due to the heterogeneous nature of the system. There are four rate coefficients, $k_{i,j}$ for each type of species entry, transfer, propagation as well as termination. The partition coefficients, probability for reactions, reactivity coefficients and mole fractions of these two monomers are used to calculate the average values of the rate coefficients.

3.7.1 Rate Coefficient of Volume Growth

Two different rate coefficients (K_i) of volume growth for each free radical existing in a particle are involved:

$$K_A = \frac{(k_{pAA}C_{p,A}+k_{pAB}C_{p,B})M_{w,A}}{d_{p,A}N_a} \tag{65}$$

$$K_B = \frac{(k_{pBB}C_{p,B}+k_{pBA}C_{p,S})M_{w,B}}{d_{p,B}N_a} \tag{66}$$

and the average rate coefficient of volume growth as follows:

$$K = P_A K_A + P_B K_B \tag{67}$$

3.7.2 Entry and Exit Rate Coefficients

Entry is one of the important events for nucleation, because entry competes with particle formation. There are several contributing entry events in an emulsion polymerization. Entry of z-mer into a micelle or a pre-existing particle is the major paths for entry while re-entry of an exited radical is the minor one. Re-entry is formed by transfer to monomer or chain transfer agents, into a particle or micelle. The entry processes to the particle and micelle are assumed to be diffusion controlled. Given that oligomeric radicals can only enter a micelle or pre-existing particle, the entry coefficients for monomer A and B to the micelles can be calculated by the following equations:

$$k_{e,micelle,A}^{i}(V) = 4\pi r_{micelle} Na \frac{Dw,A}{i}, for\ i \geq z; \tag{68}$$

$$k_{e,micelle,A}^{i}(V) = 0, for\ i < z; \tag{69}$$

$$k_{e,micelle,B}^{i}(V) = 4\pi r_{micelle} Na \frac{Dw,B}{i}, for\ i \geq z; \tag{70}$$

$$k_{e,micelle,B}^{i}(V) = 0, for\ i < z; \tag{71}$$

where Dw is the diffusity coefficient of the radicals in the water phase.

To get the average entry of the monomer to the micelle,

$$k_{e,micelle}^{i} = k_{e,micelle,A}^{i}.f_A.\emptyset_A + k_{e,micelle,B}^{i}.f_B.\emptyset_B \tag{72}$$

The expressions above are obeying the Smoluchowski relation, Rouse model, and Maxwell-Morrison model (Gilbert, 1995, Lovell and El-Aasser, 1997, Alhamad et al., 2005, Coen, 1999).

The entry of a z-mer into a glassy particle, at high conversion, is impeded because of slow diffusion through the interface. The secondary-order entry rate coefficients to particles and their averages are given by (Clay and Gilbert, 1995):

$$k_{e.A}^{i,j} = 4\pi r_s^j Na \frac{D_{w,A}}{i}, for\ i \geq z; \quad k_e^i(V) = 0, i < z \tag{73}$$

$$k_{e.B}^{i,j} = 4\pi r_s^j Na \frac{D_{w,B}}{i}, for\ i \geq z; \quad k_e^i(V) = 0, i < z \tag{74}$$

and the average entry of the monomer to the particle is given by,

$$k_e^{i,j} = k_{e,A}^{i}.f_A.\emptyset_A + k_{e,B}^{i}.f_B.\emptyset_B \tag{75}$$

The second-order entry rate coefficients of exit-derived radicals to the particles undergo the same assumptions as that of z-mer. The entry rate coefficients of exited radicals and their average can be defined in a similar fashion:

$$k_{eE,A}^{j} = 4\pi r_s^j N_A D_{w,A} \tag{76}$$

$$k_{eE,B}^{j} = 4\pi r_s^j N_A D_{w,B} \tag{77}$$

and the average entry of exit-derived to the particle is given by,

$$k_{eE}^{j} = k_{eE,A}^{j} + k_{eE,B}^{j} \tag{78}$$

The overall pseudo first-order rate constant of entry is defined by the following equation:

$$p^j = p^j_{init} + k_{eE}E \tag{79}$$

while

$$p^j_{init} = \sum_1^G (k_e^{(i,j)} IM_i) \tag{80}$$

where G is the number of radius increments to be integrated for.

The desorption rate coefficients of monomeric radicals into the water phase are calculated from

$$k^j_{dm} = \frac{3D_{mon}D_w}{(qD_{mon}+D_w)(r^j_s)^2} \tag{81}$$

$$q = \frac{C_p}{C_w} \tag{82}$$

3.7.3 Termination Rates

The particles with a radical could undergo termination reactions. However, they may futher be activated and propagate again, and then terminate and so on. The termination coefficient at high conversions is subjected to the gel effect and is given by,

$$k_{t,aq,A} = 1.703x10^9 e^{-\frac{2263*4.182}{RTr}} \tag{83}$$

$$k_{t,aq,B} = 9.8x10^9 e^{-\frac{701*4.182}{RTr}} \tag{84}$$

$$k_{to} = k_{t,aq,A}f_A + k_{t,aq,B}f_B \tag{85}$$

$$k_t = k_{to}g^2 \tag{86}$$

$$g^2 = (g_A^2 g_B^2)^{1/2} \tag{87}$$

$$g_A^2 = \left[\frac{1}{1-x} exp(-6.59x - 1.896x^2)\right]^2 \tag{88}$$

$$g_B^2 = [exp(-0.94x - 3.87x^2 + 0.49x^3)]^2 \tag{89}$$

while k_t the average termination coefficient in the particle phase in given by

$$k_t = k_{t,AA}P_A^2 + 2k_{t,AB}P_AP_B + k_{t,BB}P_B^2 \tag{90}$$

Asua et al.(1989) showed that termination has a significant effect on the probability of desorption for small particle sizes. The overall desorption coefficients are calculated by:

$$k_{des,A}(j) = \frac{(k_{tr,AA}P_A + k_{tr,BA}P_B)C_{p,A}k_{o,A}}{\beta_A(j)k_{oA} + k_{pAA}C_{p,A} + k_{pAB}C_{p,B}} \tag{91}$$

$$k_{des,B}(j) = \frac{(k_{tr,AB}P_A + k_{tr,BB}P_B)C_{p,B}k_{o,B}}{\beta_B(j)k_{oB} + k_{pBA}C_{p,A} + k_{pBB}C_{p,B}} \tag{92}$$

$$\mathrm{k_{des}(j) = k_{des,A}(j) + k_{des,B}(j)} \tag{93}$$

3.7.4 Transfer Rate Coefficients

Transfer to monomeric radicals takes place within the particle phase since there is no transfer to polymeric radicals, since there are no transfer agents are involved in the reaction. The transfer coefficient for styrene and MMA as given by,

$$k_{tr,A} = k_{p,A}x10^{-0.658}e^{-\frac{23400}{RTr}} \tag{94}$$

$$k_{tr,B} = 4x10^{5.3}e^{-\frac{45900}{RTr}} \tag{95}$$

The average transfer coefficient is given by,

$$k_{tr} = k_{tr,AA}P_A^2 + k_{tr,AB}P_AP_B + k_{tr,BB}P_B^2 + k_{tr,,BA}P_BP_A \tag{96}$$

3.7.5 Propagation Rate Coefficients

Propagation is the fundamental reaction in any polymerization. Under most conditions propagation is not diffusion-controlled. However, at high monomer conversion, the viscosity inside the polymer particles increases sharply and further polymerization becomes diffusion controlled. Hence, in a glassy system diffusion does become rate-determining for propagation at high conversion. Propagation rate coefficient depends significantly on chain length for short chains of oligomers (Gilbert, 1995). One reason for this arises because the hindered rotations which characterize the transition state for propagation are influenced by the degree of polymerization of oligomers. The propagation constant for monomer A and B at low conversion are given as follows;

$$k_{po,A} = 10^{7.63} e^{-\frac{32500}{RTr}} \tag{97}$$

$$k_{po,B} = 10^{6.4} e^{-\frac{22200}{RTr}} \tag{98}$$

These propagation coefficients are diffusion controlled at high conversion and are given by,

$$\frac{1}{k_{p,A}} = \frac{1}{k_{po,A}} + \frac{1}{k_{diff,A}} \tag{99}$$

$$\frac{1}{k_{p,B}} = \frac{1}{k_{po,B}} + \frac{1}{k_{diff,B}} \tag{100}$$

Where $k_{diff,A}$ and $k_{diff,B}$ are the diffusion controlled rate coefficient defined as:

$$k_{diff,A} = 4\pi\sigma N_A\left(D_{mon,A} + D_{rd,A}\right) \tag{101}$$

$$k_{diff,B} = 4\pi\sigma N_B\left(D_{mon,B} + D_{rd,B}\right) \tag{102}$$

where

$$D_{rd,A} = \frac{1}{6} k_{p,A} C_{p,A} \propto^2 \tag{103}$$

$$D_{rd,B} = \frac{1}{6} k_{p,B} C_{p,B} \propto^2 \quad (104)$$

The diffusion coefficients for styrene and MMA decrease at high conversion and this in turn results in the decrease of the propagation and termination coefficients. Diffusion coefficients as functions of polymer volume fractions are given as

$$D_{mon,A} = 10^{0.417-29.51\varphi_{p,A}+53.14\varphi_{p,A}^2-36.03\varphi_{p,A}^3} for\ \varphi_{p,A} < 0.8 \quad (105)$$

$$D_{mon,A} = 9x10^{-8} e^{-19.16\varphi_p} for \varphi_{p,A} \geq 0.8 \quad (106)$$

$$D_{mon,B} = 10^{-4.386-3.2\varphi_{p,B}+9.049\varphi_{p,B}^2-12.079\varphi_{p,B}^3} for\ \varphi_{p,B} < 0.8 \quad (107)$$

$$D_{mon,B} = 75.651 e^{-42.271\varphi_{p,B}} for \varphi_p \geq 0.8 \quad (108)$$

Thus, the entry of a z-mer into glassy particle is impeded due to slow diffusion at the interface at high φ_p. The foiled z-mer then desorbs back into the aqueous phase and may propagate to a j_{crit}-mer and cause secondary nucleation. A semi-empirical equation for the entry efficiency $e_e = ((1-\varphi_p)^{C_{p,sat}})$ is used to model this effect. Further, the degree of propagation coefficients are given by

$$k_{p,aq,A}^1 = 2k_{p,A} \quad (109)$$

$$k_{p,aq,A}^2 = 1.753k_{p,A} \quad (110)$$

$$k_{p,aq,A}^3 = k_{p,A} \quad (111)$$

$$k_{p,aq,B}^1 = 3.15k_{p,B} \quad (112)$$

$$k_{p,aq,B}^2 = 2k_{p,B} \quad (113)$$

$$k_{p,aq,B}^3 = k_{p,B} \quad (114)$$

$$k_{p,aq}^i = k_{p,aq}^3 \quad (115)$$

k_{pBA},k_{pAB} are the propagation coefficients when A propages with B, and B propagates with A respectively, and they can obtained by the following relations:

$$k_{pAA} = k_{p,aq,A}^1 \quad (116)$$

$$k_{pBB} = k_{p,aq,B}^1 \quad (117)$$

$$k_{pAB} = \frac{k_{pAA}}{r_A} \tag{118}$$

$$k_{pBA} = \frac{k_{pBB}}{r_B} \tag{119}$$

k_{pAA}, k_{pBB} are the propagation coefficients when A propagates with A and B propagates with B, respectively, and r_A and r_B are the reactivity ratios for monomer A and B respectively.

The average propagation coefficient is given as

$$k_{p,aq}^{i} = k_{p,aq,A}^{i}.f_A.\emptyset_A + k_{p,aq,B}^{i}.f_B.\emptyset_B \tag{120}$$

The probabilities for oligomeric radicals to propagate or terminate in the particle phase are defined as follows:

$$P_A = \frac{k_{pBA}C_{p,A}}{k_{pBA}C_{p,A}+k_{pAB}C_{p,B}} \tag{121}$$

$$P_B = 1 - P_A \tag{122}$$

The average propagation coefficient in the particle phase is calculated by,

$$k_p = k_{pAA}.P_A^2 + K_{pAB}.P_A.P_B + k_{pBA}.P_B.P_A + k_{pBB}.P_B^2 \tag{123}$$

3.7.6 Exit of monomeric radical from polymer particles rate coefficients

The rate of exit of a monomeric radical of type I from the polymer particles, k_{oi} can be determined by equation below by assuming a diffusion mechanism and no additional resistance at the interface,

$$k_{o,A} = \frac{12D_{w,A}/K_{A,wp}d^2}{1+2D_{w,A}/K_{A,wp}D_{p,A}} \tag{124}$$

$$k_{o,B} = \frac{12D_{w,B}/K_{B,wp}d^2}{1+2D_{w,B}/K_{B,wp}D_{p,B}} \tag{125}$$

Where $D_{w,A}$ and $D_{p,A}$ are the diffusion coefficients of a monomeric radicals of type I in the aqueous phase and the polymer particles, respectively. $K_{a,wp}$ is the partition coefficient of such a radical between polymer particles and the aqueous phase, and d is the diameter of the particles.

3.7.7 Efficiency of Initiator Dissociation Constant

The efficiency dissociation constant of initiator is calculated through the following equation (Gilbert, 1995).

$$f = (\frac{(k_d[I]k_{t,aq})^{0.5}}{k_{p,aq}C_w} + 1)^{(1-z)} \tag{126}$$

The following equations represent the dissociation of the initiator and the decomposition coefficient, k_d(1/mol.s) of the :

$$k_d = 8x10^{15}e^{\frac{135000}{RT_r}} \tag{127}$$

3.8 Physical Parameters

3.8.1 Average Density and Molar Fraction

The average densities of the monomers, d_{avg}, and that of the polymer, d_p, are estimated by:

$$d_{avg} = f_A d_{m,A} + f_B d_{m,B} \tag{128}$$

$$d_p = f_A d_{p,A} + f_B d_{p,B} \tag{129}$$

The average molecular weight is given by:

$$M_w = f_A M_{w,A} + f_B M_{w,B} \tag{130}$$

The molar fractions of monomers in the reaction system are given as follows:

$$f_A = \frac{N_{m,A}^{fed}}{N_{m,A}^{fed} + N_{m,B}^{fed}} \tag{131}$$

$$f_B = 1 - f_A \tag{132}$$

Where Na is Avogadro's number, $N_{m,A}^{fed}$and $N_{m,B}^{fed}$are the number of moles fed for A and B , $\emptyset_A$and $\emptyset_B$ are the probability of the reaction of radicals A and B in the water phase.

The polymer molar fractions of styrene and MMA are

$$F_{bar,A} = \frac{N_{pol,A}}{N_{pol,A} + N_{pol,B}} \tag{133}$$

$$F_{bar,B} = \frac{N_{pol,B}}{N_{pol,A} + N_{pol,B}} \tag{134}$$

3.8.2 Conversion and Polymer Volume Fraction

It is important to predict the conversion of the process since conversion accuracy provides a reasonable test of the kinetic model. It is also important in recipe design, for example to allow sufficient time for heat dissipation in large-scale reactions or for time to take samples in small scale reactions. According to the dynamic model, the conversion of monomer A(x_A)and monomer B(x_B) to a copolymer is given by,

$$x_A = 1 - \frac{N_{m,A}}{N_{m,A}^{fed}} \tag{135}$$

$$x_B = 1 - \frac{N_{m,B}}{N_{m,B}^{fed}} \tag{136}$$

and the overall conversion is as follows:

$$x = \frac{x_A M_{w,A} + x_B M_{w,B}}{M_{w,A} + M_{w,B}} \tag{137}$$

The polymer volume fraction inside the particle, φ_p , is another indication of the particle status at any time. It can be predicted from the monomer concentration inside the particle as follows,

$$\varphi_p = 1 - \frac{C_p M_{avg}}{d_{avg}} \tag{138}$$

3.9 Parameter for simulating styrene and MMA copolymerization

The model parameters used for simulation include the reaction rate coefficients for propagation, transfer and termination, surfactant and initiator physical properties, for styrene and MMA showed in Table 2 below while the feed in rate showed in Table 3.1.

Table 3.1 Parameters for Simulating Styrene and MMA Copolymerization

Parameter	Styrene	MMA
k_{po}	$k_{po,A}=10^{7.63}e^{-12200/RTr}$	$k_{po,B}=10^{6.4}\, e^{-22200/RTr}$
k_{tr}	$k_{tr,A}=k_{p,A}\, 10^{-0.658}e^{-23400/RTr}$	$k_{tr,B}=4x10^{5.3}\, e^{-45900/RTr}$
k_{to}	$k_{to}=k_{t,aq,A}f_A+k_{t,aq,B}\, f_B$	$k_{to}=k_{t,aq,A}\, f_A+k_{t,aq,B}\, f_B$
$K_{t,aq}$	$k_{t,aq,A}=1.703x10^9e^{-2263*4.182/RTr}$	$k_{t,aq,B}=9.88x10^7e^{-701*4.182/RTr}$
d_p	1050.1-0.621T	1.178
d_m	923.6-0.887T	0.909
z	3	5
j_{crit}	5	10
k_{mwp}	C_{w_sat}/C_{p_sat}	C_{w_sat}/C_{p_sat}
$\boldsymbol{k^1_{p,aq}}$	$k^1_{p,aq,A} = 2k_{p,A}$	$k^1_{p,aq,B} = 3.15k_{p,B}$
$\boldsymbol{k^2_{p,aq}}$	$k^2_{p,aq,A} = 1.753k_{p,A}$	$k^2_{p,aq,B} = 2k_{p,B}$
$\boldsymbol{k^3_{p,aq}}$	$k^3_{p,aq,A} = k_{p,A}$	$k^3_{p,aq,B} = k_{p,B}$
$\boldsymbol{k^4_{p,aq}}$	$k^i_{p,aq} = k^3_{p,aq}$	$k^i_{p,aq} = k^3_{p,aq}$
D_w	$1.55x10^{-7}$	$1.7x10^{-7}$
M_o	0.04	0.101
C_{p_sat}	5.5	6.6

Table 3.1 Continued

C_{w_sat}	exp(-1.514-1259/(T+273)	0.15
CMC	$3x10^{-3}$	$3x10^{-3}$
n_{agg}	60	60
a_s	$42x10^{-18}$	$42x10^{-18}$
σ	$0.602x10^{-8}$	$0.602x10^{-8}$

Chapter 4

Dynamic Optimization Problem Formulation

The objectives functions were first defined as previous chapter. For operational and technical reasons such as the specified conversion, feed rates of monomers, surfactant and initiator, and the temperature as well as diameter of particle were specified within upper and lower bounds.

4.1 Maximization of Number Average Molecular Weight Problem (M_n)

The optimization problem can be described as :

Given *Fixed diameter of particle* (D_{mm})*, Fixed total amount of monomer* ($N_{m,T}$) *feed , Fixed pre-batch time* (t_{bp})*, Fixed final batch time*

Optimize *Styrene feed rate* (F_{mA})*, MMA feed rate* (F_{mB})*, Surfactant feed rate* (F_S)*, Initiator feed rate* (F_I)*, Jacket temperature* (T_{jo})*, Controller switching times*

So as to maximize *Number Average Molecular Weight* (M_n)

Subject to constraint *Model equations, Linear bounds on:*

Initial Iniator concentration (C_{Io})*, Initial Surfactant concentration* (S_o)*, Initial styrene concentration* ($F_{mA,o}$)*, Initial MMA* *concentration ($F_{mB,o}$), Reactor temperature (T_r), Copolymer composition*

Mathematically the optimization problem for minimum time problem can be described as;

$$\underset{F_{mA}(t);F_{mB}(t);F_S(t);F_I(t);T_{jo}}{\text{Max}} \quad M_n$$

s.t. $f(t, x'(t), x(t), u(t), v) = o, [t_o, t_f]$ [model equations]

$$F_{mA}^l < F_{mA} < F_{mA}^u \quad ; \quad F_{mB}^l < F_{mB} < F_{mB}^u$$

$$F_S^l < F_S < F_S^u \quad ; \quad F_I^l < F_I < F_I^u$$

$$T_r^l < T_r < T_r^u \quad ; \quad D_{mm}^l < D_{mm} < D_{mm}^u$$

$$N_{m,T} = N_{m,T}^*$$

The subscript l and u referred to lower and upper bounds. To maximize the overall conversion, M_n, the styrene feed rate(F_{mA}), MMA feed rate(F_{mB}), surfactant feed rate(F_s), initiator feed rate(F_I), jacket temperature(T_{jo}) will be optimized.

4.2 Maximization of Overall Conversion Problem (X_n)

The optimization problem can be described as :

Given *Fixed diameter of particle (D_{mm}), Fixed total amount of monomer ($N_{m,T}$) feed, Fixed molecular weight (M_n) , Fixed pre-batch time (t_{bp}), Fixed final batch time*

Optimize *Styrene feed rate (F_{mA}), MMA feed rate (F_{mB}), Surfactant feed rate (F_S), Initiator feed rate (F_I), Jacket temperature (T_{jo}), Controller switching times*

So as to maximize *Overall conversion(X_n)*

Subject to constraint *Model equations.Linear bounds on:*

Initial Iniator concentration (C_{Io}), Initial Surfactant concentration (S_o), Initial styrene concentration ($F_{mA,o}$), Initial MMA concentration ($F_{mB,o}$), Reactor temperature (T_r), Copolymer composition

Mathematically the optimization problem for minimum time problem can be described as;

$$\underset{F_{mA}(t); F_{mB}(t); F_S(t); F_I(t); T_{jo}}{\text{Max}} \quad X_n$$

s.t. $f(t, x'(t), x(t), u(t), v) = o, [t_o, t_f]$ [model equations]

$$M_n = M_n^*$$

$$F_{mA}^l < F_{mA} < F_{mA}^u \quad ; \quad F_{mB}^l < F_{mB} < F_{mB}^u$$

$$F_S^l < F_S < F_S^u \quad ; \quad F_I^l < F_I < F_I^u$$

$$T_r^l < T_r < T_r^u \quad ; \quad D_{mm}^l < D_{mm} < D_{mm}^u$$

$$N_{m,T} = N_{m,T}^*$$

The subscript l *and* u referred to lower and upper bounds. To maximize the overall conversion, X_n, the styrene feed rate(F_{mA}), MMA feed rate(F_{mB}), surfactant feed rate(F_S), initiator feed rate(F_I), jacket temperature(T_{jo}) will be optimized.

Control vector Parameterization (CVP), a standard mathematical solver for optimization in gPROMS, is implemented to solve the model based optimization problem in this work. CVP can solve optimization problems with both discrete and continuous decision variables. For dynamic optimization problems, CVP approach which assumes that the time-varying control variables are piecewise constant (or piecewise linear) functions of time over a specified number of control intervals. The precise values of the controls over each interval, as well as the duration of the latter, are generally determined by the optimization algorithm.

4.3 Case Study 1: Maximize Molecular Weight (M_n) for Different Pre-batch Time

In this section the computation of different pre-batch time to reach a maximum number average molecular weight (M_n) was discussed. The pre-batch time has been selected as the manipulated variable, because it has the major effect on number average molecular weight and overall conversion. The pre-batch was set at 900s, 1200s, 1500s and 1800s to maximize the number average molecular weight as well as overall conversion in each process respectively.

Max M_n

$F_{mA}(t); F_{mB}(t); F_S(t); F_I(t); T_{jo}$

s.t. $f(t, x'(t), x(t), u(t), v) = 0, [t_o, t_f]$ [Model equations]

$$t_{pb} = t_{pb}^{*} \quad ; \quad t_f = 5000s$$

$$0.0g/s < F_S < 0.2g/s \quad ; \quad 0.0g/s < F_I < 0.2g/s$$

$$343.00K < T_r < 358.00K \quad ;$$

$$0.4x10^{-7}m < D_{mm} < 9.0x10^{-7}m \quad ;$$

$$N_{m,T} = 8\,mol$$

4.4 Case Study 2: Maximize X$_n$ In Batch Process with Fixed Pre-Batch Time

In this section the computation of number average molecular weight (M$_n$) for fixed final batch time 5000s for reaching a desired overall conversion (X$_n$) is discussed. The number average molecular weight has been selected as the manipulated variable, because it has the major effect on overall conversion. The average molecular weight was set at 50 000 g/mol, 100 000 g/mol, 150000 g/mol and 200 000 g/mol to maximize the overall conversion in each process respectively.

Max X_n

$F_{mA}(t); F_{mB}(t); F_S(t); F_I(t); T_{jo}$

s.t. $f(t, x'(t), x(t), u(t), v) = 0, [t_o, t_f]$ [Model equations]

$$M_n = M_n^* \quad ; \quad t_f = 5000s$$

$$0.0g/s < F_S < 0.2g/s \quad ; \quad 0.0g/s < F_I < 0.2g/s$$

$$343.00K < T_r < 358.00K \quad ;$$

$$0.4x10^{-7}m < D_{mm} < 9.0x10^{-7}m \quad ;$$

$$N_{m,T} = 8\,mol$$

4.5 Case Study 3: Maximize X_n In Batch Process with Different Pre-Batch Time

In this section the computation of different pre-batch time (t_{pb}) for different molecular weight for reaching a desired overall conversion (X_n) is discussed. The pre-batch time has been selected as the manipulated variable, because it has the major effect on overall conversion. The pre-batch time was set at 1200s and 1500s. The average molecular weight which used to test for different pre-batch time was set at 100 000 g/mol, 150000 g/mol and 200 000g/mol to maximize the overall conversion in each process respectively.

Max X_n

$F_{mA}(t); F_{mB}(t); F_S(t); F_I(t); T_{jo}$

s.t. $f(t, x'(t), x(t), u(t), v) = 0, [t_o, t_f]$ [Model equations]

$$M_n = M_n^*$$

$$0.0g/s < F_S < 0.2g/s \quad ; \quad 0.0g/s < F_I < 0.2g/s$$

$$343.00K < T_r < 358.00K \quad ;$$

$$0.4x10^{-7}m < D_{mm} < 9.0x10^{-7}m \quad ;$$

$$N_{m,T} = 8\, mol$$

4.6 Case study 4: Maximize X_n in Batch Process with Different Batch Time

In this section the computation of different batch time to reach a maximum number average molecular weight (M_n) was discussed. The batch time has been selected as the manipulated variable, because it has the major effect on number average molecular weight and overall conversion. The batch was set at 5000s, 5500s and 6000s to maximize the number average molecular weight as well as overall conversion in each process respectively.

Max X_n

$F_{mA}(t); F_{mB}(t); F_S(t); F_I(t); T_{jo}$

s.t. $f(t, x'(t), x(t), u(t), v) = o, [t_o, t_f]$ [Model equations]

$$t_{bt} = t_{bt}^*$$

$$0.0g/s < F_S < 0.2g/s \quad ; \quad 0.0g/s < F_I < 0.2g/s$$

$$343.00K < T_r < 358.00K \quad ;$$

$$0.4x10^{-7}m < D_{mm} < 9.0x10^{-7}m \quad ;$$

$$N_{m,T} = 8\, mol$$

CHAPTER 5

RESULTS AND DISCUSSION

Styrene monomer (410.40g), MMA monomer (410.40g), Initiator (l.875g), Surfactant (5.39g), and water (2.5 L) were chosen used for the simulation of the emulsion polymerization model for both case studies below. The surfactant and the initiator chosen in this study is the Sodium Dodecyl Sulfate (SDS) and Potassium Persulfate $K_2S_2O_8$ respectively.

5.1 Case Study 1: Maximize Molecular Weight (M_n) for Different Pre-batch Time

Table 5.1: Summary of Maximize Molecular Weight (Mn) for Different Pre-batch Time

Run	M_n	X_n(%)	D_{mm}(nm)	Pre-batch time (s)
1	1503,157	95.77	87.0	900
2	1500,157	96.08	87.3	1200
3	1500,153	96.61	88.3	1500
4	1499,981	98.06	88.5	1800

Pre-batch time is the time for a seed population with a smaller particle and larger size particles are produced. As pre-batch time increase, the particle size of the particle can be produced increase but the average number molecular weight (M_n) is decrease with increase in overall conversions. This results show that the maximum molecular weight 1503,157 g/mol can be achieved with overall conversion 95.77%. This result clearly shows that to maximize the molecular weight (M_n), pre-batch time can be reduced although it is needed in the process. The overall conversion of monomer have been increase with increase of pre-batch time as the monomer as the longer pre-batch time leads the shorter processing time for fixed batch time. The likelihood to the monomer added the process to reactant and the entry of polymer chain inside the particle are larger for longer processing time (shorter pre-batch time).

Figure 5.1 shows the optimization result of Run 3, which is 1500s of pre-batch time. It can be seen that the temperature will remain high until 3250s before it goes down to 343 K when the reaction stop. The radical transfer in the polymerization process will increase at high temperature consequently lead to shorter chains of polymer (low M_n) as shown in Figure 5.1(a). The decrease of temperature will lead the increase of polymer chains (the molecular weight) so that it can achieve to the maximum molecular weight. The surfactant feed rate is 0.01g/s, a very slow feed rate. It is just used to stabilize the particle formed which is larger, so that there are no new micelles produced for micelles nucleation. It is only some initiator added along the process, from 2250s until 3250s. The addition of initiator can reduce the molecular weight.

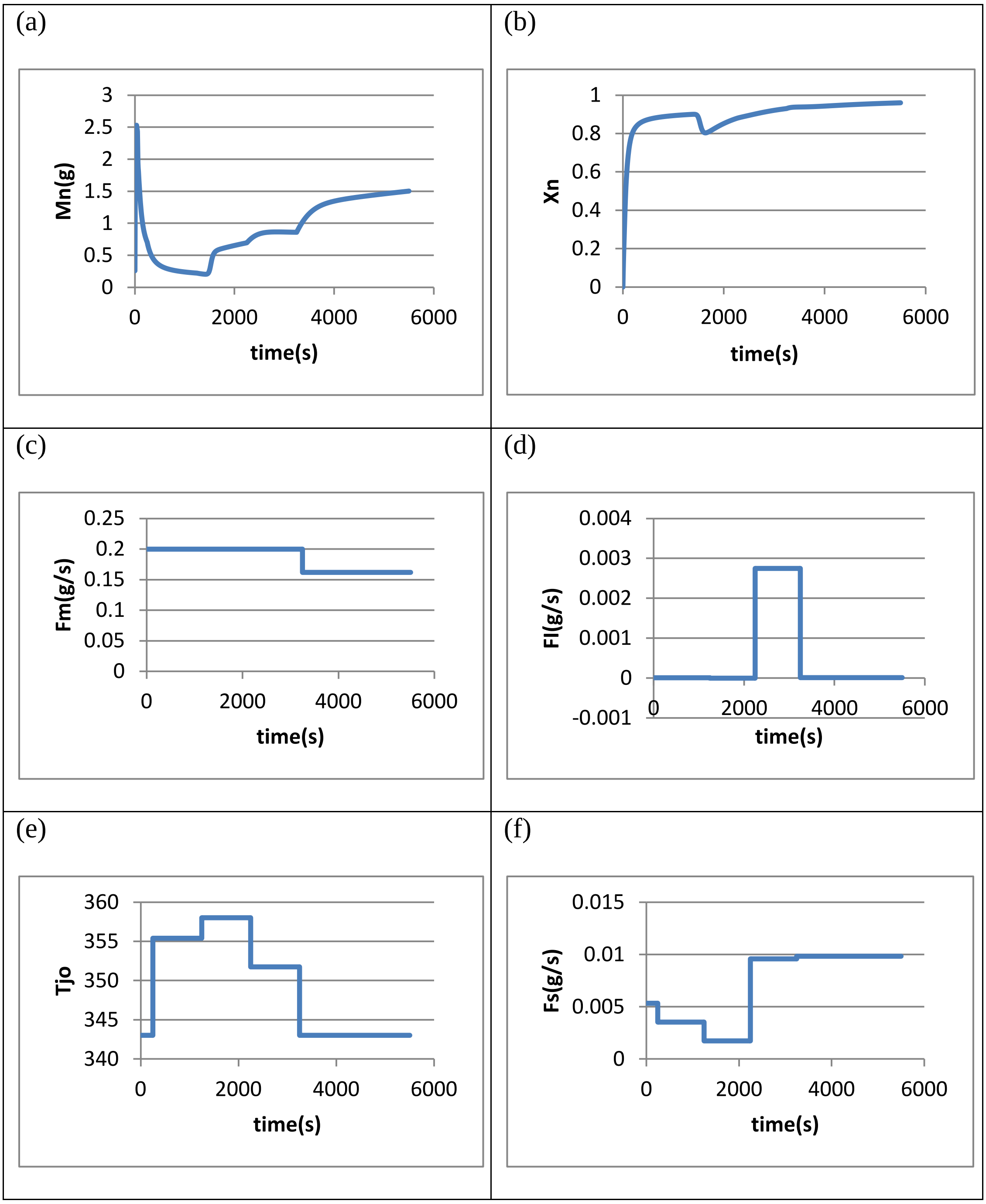

Figure 5.1: Case Study 1 (Run 3); Optimization result (a) number average molecular weight(M_n); (b) overall conversion (X_n);(c) optimal profile of monomer flow rate; (d) optimal profile of initiator flow rate; (e) optimal profile of jacket temperature(T_r); (f) optimal profile of surfactant flow rate(F_s)

5.2 Case Study 2: Maximize X_n In Batch Process with Fixed Pre-Batch Time

Table 5.2 showed the results for maximization of X_n in batch reactor. From the table, the results show that the overall conversion achieve highest, 97.21% at number average molecular weight 100 000 g/mol. Anyway, the overall conversion for other number average molecular weight is achieved around 96%, nearer with the highest overall conversion. The X_n for run 1 is slightly lower than the rest because there is more initiator was used in the process if compared with Run 2, 3 and 4.

Table 5.2: Results For Maximization of X_n In Batch Reactor.

Run	M_n	M_n*	X_n
1	50 050	50 000	95.88
2	100 043	100 000	97.21
3	150 015	150 000	96.61
4	199 996	200 000	96.40

From Figure 5.2 below, it showed that the number of average molecular weight for 50 000 g/mol is lower than the rest (Figure 5.2(a)) when the initiator concentration is increase at 1600s (Figure 5.2(d)).It is due to the monomer is used up to react with the initiator to initiate the polymerization process rather than continue to propagate with the oligomeric radicals. The lower molecular weight then makes the monomer conversion for Run 1 is decrease in the process as shown in the Figure 5.2(b).

In the optimization process, the temperature was increased to decrease the average molecular weight (Figure 5.2(c)). It is due to the increasing of the temperature will decrease the chain length due to the kinetic transfer event. Higher temperatures happen when initiation occurs by thermal decomposition of the initiator. The entry radicals to the particles would result in instantaneous termination. Free surfactant concentration has important role in the nucleation and consequently affects the total number of particles. Flow rate of surfactant is increased in the process to achieve to the desired molecular weight as the added surfactant produced new particles by micellar nucleation (Figure 5.2(f)). The flow rate of monomer fed is keep constant in the process and decrease at the end of process due to the sufficient of the monomer to change to the polymer latex (Figure 5.2 (e)). The flow rate of monomer for 50 000 g/mol is decrease to zero at 850s until 1500s. It is due to the increasing of the initiator to the reactor.

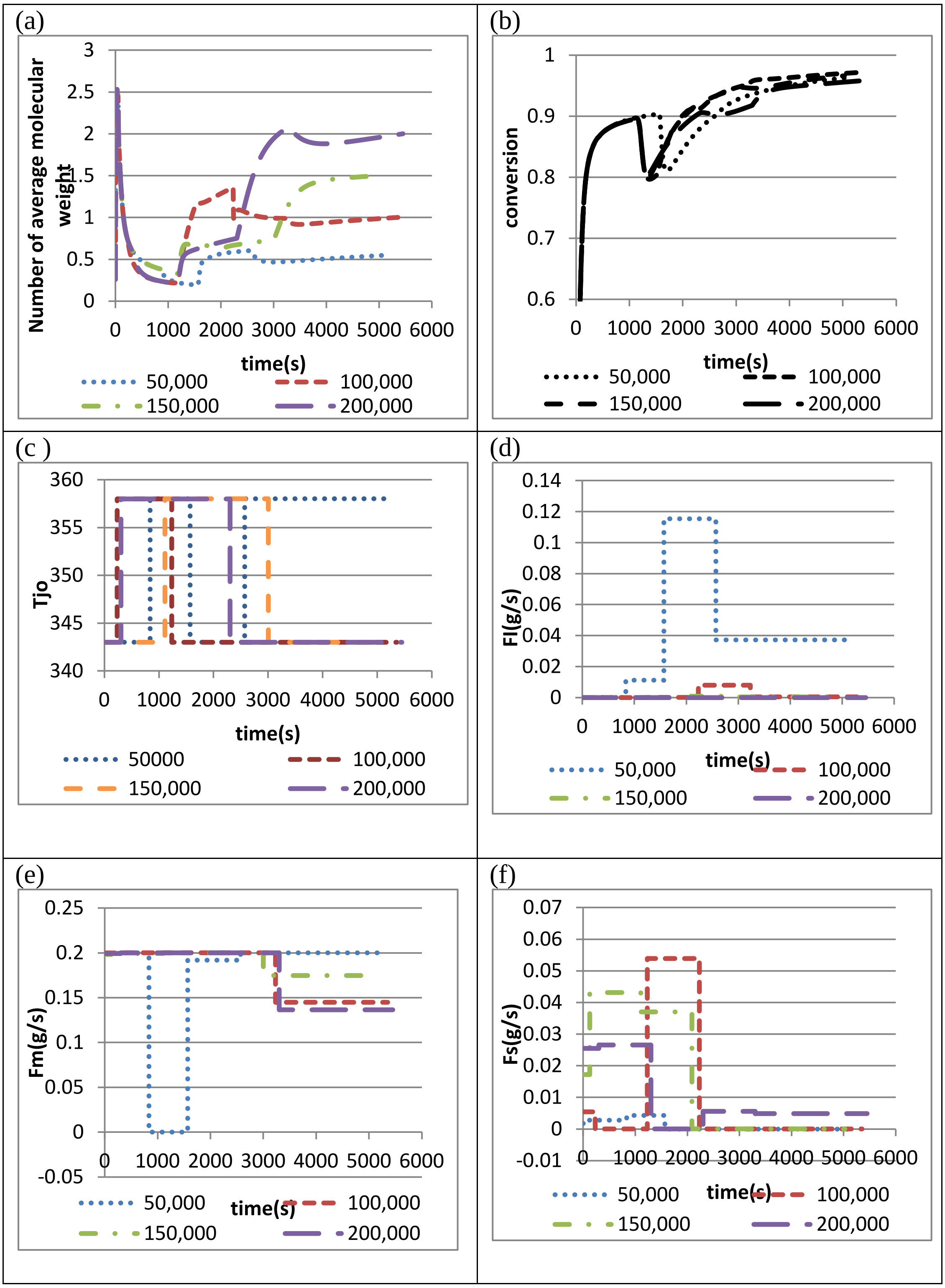

Figure 5.2: Result Case Study 2 : (a)Number average molecular weight (b) overall conversion (c) optimal profile of jacket temperature (d) optimal profile of initiator flow rate (e) optimal profile of monomer flow rate(Fm) (f) optimal profile of surfactant flow rate (Fs)

5.3 Case study 3: Maximize X_n in Batch Process with Different Pre-batch Time

Table 5.3 and Table 5.4 showed the maximum overall conversion for number average molecular weight of 100,000 g/mol, 150,000 g/mol and 200,000 g/mol with pre-batch time 1200 and 1500 s respectively.

Table 5.3: Summary of the results with pre-batch time 1200s

M_n*	M_n	X_n(%)
100, 000	99,997	97.21
150,000	150,015	96.61
200,000	199,996	95.88

Table 5.4 :Summary of the results with pre-batch time 1500s

M_n*	M_n	X_n (%)
100,000	100,043	96.45
150,000	150,349	96.07
200,000	200,001	95.65

From both of the table above, the results proved that, a higher conversion can be achieved in shorter time with desired molecular weight. For instance, for 150,000 g/mol number average molecular weight, the conversion for pre-batch time 1200s is 0.56% higher if compared with the result of pre-batch time 1500s. It is because the shorter the pre-batch time, the sooner the monomer are added into the reactor and increase the likelihood to increase polymer chain length. The numbers of particles being produced are larger for longer pre-batch time. The molecular weights in Table 5.4 are larger than the molecular weights in Table 5.3. The summary of percentage difference of X_n for 2 pre-batch time are shown in Table 5.5 below.

Table 5.5: Percentage (%) Difference of Xn between 2 Pre-batch Time

M_n*	X_n(%) for pre-batch time 1200s	X_n(%) for pre-batch time 1500s	Percentage(%) difference of Xn between 2 batch time
100,000	97.21	96.45	0.78
150,000	96.61	96.07	0.56
200,000	95.88	95.65	0.24

From table 5.4, it observed that the percentage (%) difference of X_n between 2 batch time is very small, less than 1 %. The larger the molecular weight, the smaller the overall conversion, it is due to the restricted of formation of new polymer chain. Consequently the polymer chains in propagation will continue to grow to give higher number average molecular weight but lower overall conversion (X_n) of the monomer.

5.4 Case study 4: Maximize X_n in Batch Process with Different Batch Time

Table 5.6 : Maximize X_n with Different Batch Time

Run	M_n(g.mol)	X_n(%)	Batch time(s)
1	1512,088	95.97	5000
2	1503,491	96.07	5500
3	1500.317	96.66	6000

The number average molecular weight decrease for longer batch time as there is more time for the monomer radicals to absorb or desorb from one particle to another particle in polymerization loci. The likelihood of polymer chain inside the particle increase and consequently, the overall conversion of monomer increase.

Figure 5.3 shows the optimization result of run 3 for number average molecular weight 15,000 g/mol for batch time 6000s. There is no surfactant added into the reactor and the jacket temperature of the reactor constant at 343K. Surfactant didn’t add in the process to prevent the produce of new particles by micellar nucleation. It shows that lower number average molecular weight (M_n) and higher overall conversion (X_n) can be achieved in longer batch process. For longer batch process, more monomer will react with the initiator to initiate the polymerization process rather than continue to propagate with oligomeric radicals.

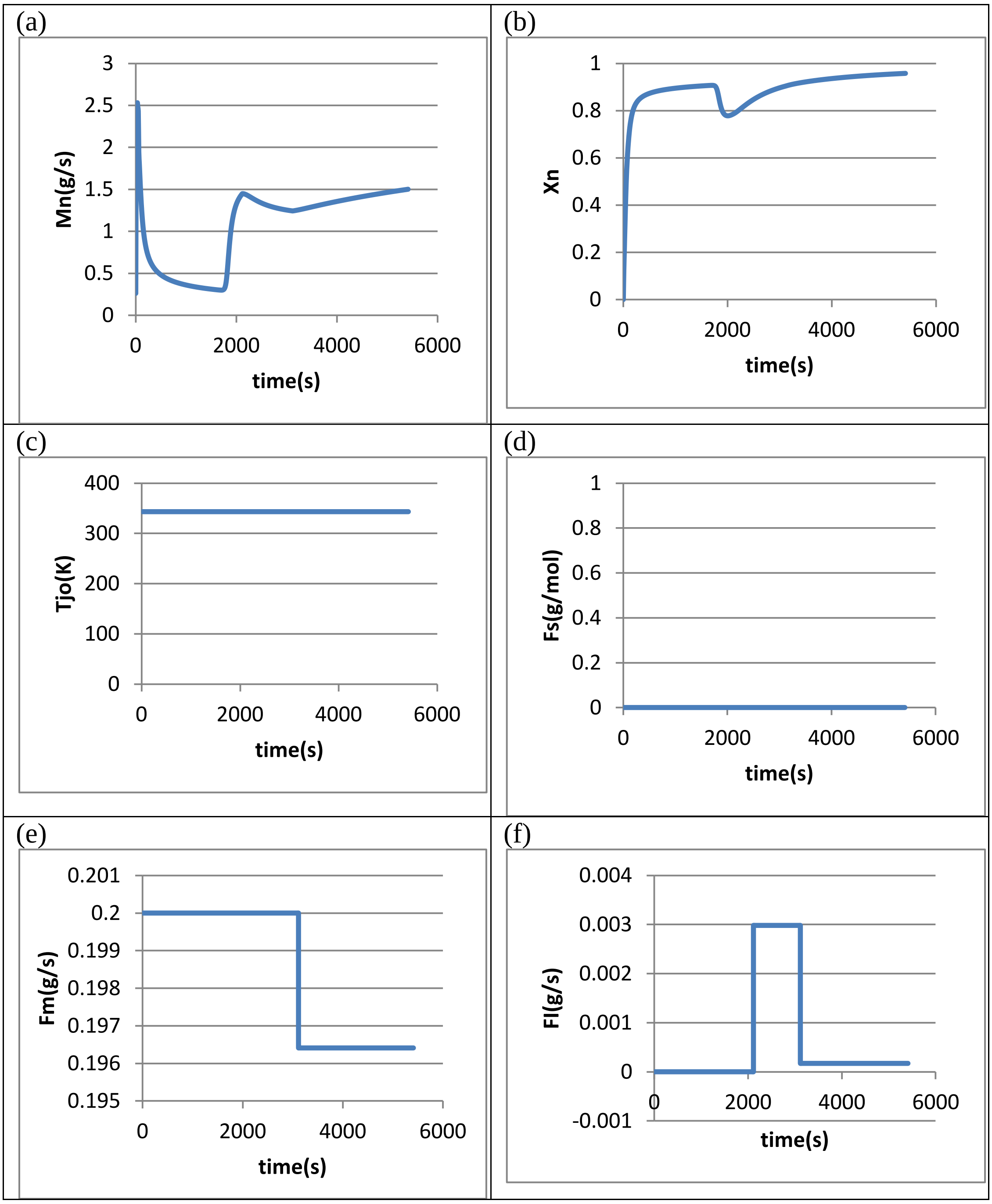

Figure 5.3: Result Case Study 4 (Run3) : (a)Number average molecular weight (b) overall conversion (c) optimal profile of jacket temperature (d) optimal profile of surfactant flow rate(Fs) (e) optimal profile of monomer flow rate(Fm) (f) optimal profile of initiator flow rate (FI)

CHAPTER 6

CONCLUSION AND RECOMMENDATION

This work focuses on the development of a dynamic model for emulsion polymerization process design and control. Good understanding to the polymer chemistry and parameters which can affect the final product quality is required for optimization of emulsion polymerization process.

For the case study 1, the results show that the maximum molecular weight 1503,157 g/mol can be achieved with overall conversion 95.77% .This result clearly shows that to maximize the molecular weight (M_n), pre-batch time can be reduced although it is needed in the process.

From the case study 2, the result shown that the overall conversion for desired molecular weight is achieved around 97%. The molecular weight increases with the number of polymer particles and the concentration of monomer in the polymer particles, and decreases as initiator concentration increases. In addition, because the activation energy of the initiator decomposition rate constant is greater than that of propagation, the molecular weights decrease with temperature.

From the case study 3 by reduced pre-batch time, the desired molecular weight and higher conversion can be achieved. It is due to the monomer can be added earlier in the reactor, consequently increase the polymer chain length (i.e higher M_n).

For the case study 4 which study the overall conversion of the process with different batch time, it can concluded that the number average molecular weight decrease for longer batch time as there is more time for the monomer radicals to absorb or desorb from one particle to another particle in polymerization loci. The likelihood of polymer chain inside the particle increase and consequently, the overall conversion of monomer increase.

It is recommended to develop the emulsion polymerization model in other monomer operations, for instance the butyl acrylate (BuA) / acrylic acid (AA) and study the differences between the models. Other product properties such as the polymer composition and particle size distribution (PSD) can the objectives of the future study. In this model, there is not included the mechanical, physical and chemical properties of the product. If there is a model developed to compute all of those properties and their relations with each other, it will be a worthy indicative.

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