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Toolbox for generation of nonlinear control models for semi-batch emulsion polymerization reactors

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I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology

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18.06.11 Anette Hoel Helgesen

Preface

This master thesis was written during the spring of 2011 as a compulsory part of the study program leading to a Master of Science degree in Chemical Engineering at the Norwegian University of Science and Technology (NTNU). The thesis work has allowed me to learn about modeling of semibatch emulsion polymerization processes. As I never had worked with polymers and polymerization I have learned a lot about these processes. I have had a great learning profit.

I would first like to thank Cybernetica for this project and Peter Singstad for being my co-supervisor. I have learned a lot from Peter Singstad, and he has been positive and supporting through my work. I spent most of the time at Cybernetica (Fossegrenda, Trondheim) and therefore had the pleasure of getting to know the employees in Cybernetica. A special thanks to Ruben Køste Ringset at Cybernetica for sharing his office with me, and for answering all my questions. I would next like to thank my supervisor, Professor Sigurd Skogestad at the Process Systems Engineering group at NTNU, Trondheim, for support and guidance throughout this master thesis. He has not only supported me through this master thesis, but I have had the possibility to learn from Sigurd Skogestad during my last years at NTNU. I am grateful to get to know Sigurd Skogestad, which is a great professor and always takes the time to help all his students.

Ineos gave me process data and teached me about E-PVC production, they also invited me to visit them in the start of this master thesis. I had a nice day in Porsgrunn, and it was interesting to learn about Ineos and polymerization, and seeing the plant. I would therefore like to extend my gratitude to Kari Herder Kaggerud, Kari-Anne Leth Olsen and Pål Thorsteinsen.

I would like to thank my fellow students for keeping a good spirit and healthy, fun atmosphere at our office. I would also like to thank PhD student Magnus G. Jacobsen that is both a friend and a PhD student at the Process Systems Engineering group. He has helped me with different programming problems and control problems during the last years. I wish to thank Professor emeritus Arvid Berge, which helped to find relevant literature on emulsion polymerization.

Last but definitely not least, I would like to thank my parents, Hilde Hoel Helgesen and Arne F. Helgesen, and my best friend and fiancé Torstein Kjemphol. Your love and support has been greatly appreciated throughout my years as a student.

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Abstract

The objective of this thesis was the study of emulsion polymerization and to model a complete, dynamic mathematical model of this process. Several variables that influence polymerization rate have been modeled with different methods to derive both simple and more complex models. As a result; several sub-models were collected in a library. All sub-models developed, constituted a toolbox for generation of nonlinear dynamic control models for semi-batch emulsion poly-merization reactors. If nonlinear model predictive control technology is implemented in a plant, a nonlinear model is necessary. The use of model predictive control is beneficial. However, it is time-consuming and costly to develop mechanistic models suitable for use in NMPC applications. The model development time can therefore be decreased if a predefined modular library of configurable sub-models exist.

An extensive literature search was performed, covering the emulsion polymerization process, control and modeling of this process and the challenges involved. Emulsion polymerization is a heterogeneous, multiphase, free radical polymerization process. The process is complex as nucleation, growth and stabilization of polymer particles are controlled by free radical polymerization mechanisms in combination with other colloidal phenomena. As a result emulsion polymerization was a challenge to model.

The sub-models developed were implemented in MATLAB. All files were programmed as functions to make the implementation less complex. The library consists of the sub-model, intermediate calculations and other functions required to obtain the sub-models. The obtained sub-models predict monomer concentration in all phases, polymerization rate, overall monomer conversion, radical distribution, moles of particles, polymer chain structural characteristics (e.g. number- and weight average molecular weights), reactor temperature and pressure, jacket outlet temperature, and moles initiator that had not decomposed. Model simplifications and tools utilized for numerical integration of the model have been studied. The system was stiff and a variable-order solver for stiff systems was utilized in MATLAB (ODE15s). Calculation time was rapid for this solver. The model could be solved as an ODE system, independent of sub -models. As a result, a DAE system was not considered. Three different methods for calculation of monomer concentration in the polymer particles were derived; one comprehensive method and two simpler. The radical distribution could be found from a number of balances found on moles of particles, *N(j)*, containing *j* radicals. These balances could be solved as multiple states, depending on how large *j* were defined. A new method for calculations of total moles of radicals was derived in this work. This method introduce less states in the model, as N(j) is not solves as states. For processes where the average particle number was lower than 0,5; a model simplification was found for such processes.

The sub-models derived could be utilized to produce different product grades. This was possible to perform by altering the amount of chemicals, the use of chain transfer agent, inhibitor, etc., as all these were parameters in the model. The mole and energy balances were not difficult to alter, so that they could be utilized for different reactor configurations. If emulsion polymerization with several monomers were modeled, a more comprehensive change in all sub-models had to be consistent, as equations in this work were for mono-polymerization. The sub-models developed should be suitable for nonlinear model predictive control and the library with all the sub-models works as a solid basis for further development.

All sub-models were tested on a case study; Semi-batch emulsion polymerization of poly-vinyl chloride. Various parameters had to be estimated; this became challenging as the model was too thorough compared to available measured values. The heat transfer coefficient was estimated with *lsqcurvefit*that is a part of the Optimization toolbox in MATLAB, and other parameters were estimated with trial-and-error. The predicted values for the outlet cooling jacket temperature and conversion were in acceptable agreement with measured values. The predicted pressure in Interval I and II had a reasonable match with the measured values in these intervals. Deviation occurred between predicted and measured pressure in interval III; there can be different explanations for this deviation. Predicted average number of radicals per particle was in the range found in literature, and the other predictions in the model were reasonable. The new method derived for the radical distribution gave the same predictions as solving *N(j)* as states, and the new method is recommended for modeling emulsion polymerization processes. The model was validated utilizing measured values from two batch processes, with different temperature profile and recipe. The predictions were acceptable for both batches.

Contents

Nomenclature

Symbol	Description	Unit
$[I]_w$	Concentration of initiator in aqueous phase	mole/l
$[M]$	Monomer concentration	mole/l
$[M]_p$	Concentration of monomer in polymer particle	mole/l
$[M]_w$	Concentration of monomer in aqueous phase	mole/l
$[M]_{w,sat}$	Saturated concentration in aqueous phase at saturation level of the monomer	mole/l
$[M]_0$	Monomer concentration start	mole/l
$[P_tot]_w$	Concentration of radicals in water phase	mole/l
$[S]$	Concentration of surfactant in aqueous phase	mole/l
$[Z]_p$	Inhibitor concentration	mole/l
A_{env}	Reactor heat-transfer area to environment	m^2
A_i	Reactor inside heat-transfer area	m^2
A_j	Frequency factor	i.e l/mol,s
A_{out}	Reactor outside heat-trasnfer area	m^2
A_p	Total particle surface area	m^2
a_p	Particle surface area of one particle	m^2
a_s	Coverage degree of surfactant	m^2/mole
A_t	Reactor top heat-trasnfer area	m^2
B_i	Virial coefficient	m^3/mole
c_p	Heat capacity	J/g,K
D_n	Moles with dead chains	mole
d_p	Particle mean diameter	m
E_I	Activation energy of initiator decomposition	J/mole
E_j	Activation energy	J/mole
E_p	Activation energy of propagation	J/mole
E_t	Activation energy of termination	J/mole
$\widehat{f}$	Fugacity	Pa
f	Initiator efficiency factor	-
$F_{I,in}$	Moles of initiator in start	mole
$F_{m,in}$	Moles of monomer in start	mole
$F_{s,in}$	Moles of surfactant in start	mole
$F_{s,post-dosed}$	Rate of surfactant post-dosed	mole/s
h_0	Heat transfer coeff. from reactor wall to the jacket	W/m^2,K
h_i	Heat transfer coeff. from reaction mixture side	W/m^2,K

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Symbol	Description	Unit
I_0	Amount of initiator initial feed into reactor	mole
K1	Monomer in water solubility constant	-
k_a	Absorption coefficient	1/s
K_{aq-p}	Partition coefficients of monomer between aqueous phase and particles	-
K_{d-aq}	Partition coefficients of monomer between the monomer droplets and aqueous phase	-
k_{de}	Desorption coefficient	l/s
k_I	Initiator decomposition constant	1/s
k_p	Propagation rate coefficient	l/mole,s
k_t	Termination rate coefficient	l/mole,s
k_{tc}	Termination by combination rate constant	l/mole,s
k_{td}	Termination by disproportionation rate constant	l/mole,s
k_{tr}^{CTA}	Transfer to CTA rate constant	l/mole,s
k_{tr}^{mon}	Transfer to monomer rate constant	l/mole,s
k_{tr}^{pol}	Transfer to polymer rate constant	l/mole,s
m	Mass	g
M_0	Initial mass with monomer	g
M_g	Monomer in gas phase	g
$\overline{M_n}$	Number-average molecular weight	g/mole
M_p	Amount monomer in polymer particle	g
$\overline{M_w}$	Weight-average molecular weight	g/mole
MW_{emu}	Molecular weight of emulgator (surfactant)	g/mole
MW_i	Molecular weight of initiator	g/mole
MW_m	Molecular weight of monomer	g/mole
MW_w	Molecular weight of water	g/mole
$\overline{n}$	Mean number of radicals per particle	-
N_{CTA}	Amount of chain transfer agent	mole
N_A	Avogradros number $(6,022 \cdot 10^{23})$	molecule/mole
N_{ini}	Amount of initiator left in reactor	mole
N(j)	Number of particles containing *j* radicals	Number
$\widetilde{N_m}$	Amount of monomer introduced in the reactor	mole
N_m	Amount of monomer in reactor	mole
N_p	Number of particles in reactor	Number
N_R	Total amount of radicals	mole
$N_{reacted,monomer}$	Reacted monomer in the reactor	mole
N_{rw}	Amount of radicals in water phase	mole
P	Reactor pressure	Pa
P_c	Critical pressure	Pa
P_m^{sat}	Saturation pressure, monomer	Pa
P_n	Moles with live radicals	mole
P_w^{sat}	Saturation pressure, water	Pa
R	Gas constant	J/mole,K

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Symbol	Description	Unit
r_p	Radius of a particle	m
R_p	Polymerization rate	mole/s
S	Amount of surfactant	mole
$t_{1/2}$	Half life	s
T_c	Critical temperature	K
$T_{j,in}$	Temperature of cooling water in	K
$T_{j,out}$	Temperature of cooling water out	K
T_{met}	Temperature of metal	K
T_R	Temperature in reactor	K
T_r	Reduced temperature	K
T_{ref}	Reference temperature	K
U	Heat transfer coeff. between reactor and cooling jacket	W/m^2,K
U_a	Heat transfer coeff. to reactor environment	W/m^2,K
U_t	Heat transfer coeff. from reactor top	W/m^2,K
V	Reactor mixture volume	l
V_g	Gas volume in reactor	l
V_{md}	Volume of monomer droplets in reactor	l
V_{mp}	Volume of monomer in particle	l
v_p	Volume of one particle	m^3
V_p	Overall volume of the monomer swollen particles in reactor	l
V_{pp}	Volume of polymer in particle	l
$V_{reactor}$	Reactor volume	l
V_w	Water volume in reactor	l
W_c	Water flow rate in cooling jacket	g/s
W_g	Water in gas phase	g
W_w	Amount of water	g
x	Monomer conversion	-
x_c	Critical conveersion at which the monomer phase disappears	-
y_m	Mole fraction of monomer in vapor	-
y_w	Mole fraction of water vapor	-
α_i	activity of a substance i	-
ΔH_r	Specific reaction enthalpy	J/mole
δ_{mw}	Monomer solubility constant	-
λ_i	ith moment of dead polymer chains	-
μ_i	ith moment of live polymer radicals	-
ρ_{emu}	Density of emulgator	g/l
ρ_i	Density of initiator	g/l
ρ_m	Density of monomer	g/l
ρ_p	Density of polymer	g/l
ρ_w	Density of water	g/l
σ	Coefficient related to saturation degree of particle	-
φ_i	Volume fraction of species i	-
χ	Flory-Huggins interaction parameter	-

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List of Abbreviations

CMC	Critical micelle concentration
DAE	Differential-Algebraic equations
E-PVC	Emulsion-Poly vinyl chloride
EKF	Extended Kalman filter
FRP	Free-radical polymerization
LMPC	Linear model predictive control
MSD	Monomer sequence distribution
MW	Molecular weight
MWD	Molecular weight distribution
ODE	Ordinary differential equation
PDI	Polydispersity index
PFR	Plug flow reactor
PVC	Poly vinyl chloride
RTD	Residence time distribution
VCM	Vinyl chloride monomer

Chapter 1

Introduction

1.1 Motivation

Several aspects of modern life would be impossible without utilizing a wide range of plastics. Most often, these plastics are the product of polymerization processes, where numerous steps are required to produce the plastic. An important polymerization technology is free radical polymerization, where the reactive compound is a radical. Emulsion polymerization is one type of a free radical polymerization.

Emulsion polymerization is an important chemical industrial process utilized for production of various polymer materials, i.e. synthetic rubbers, paints, adhesives, binders, coatings and thermoplastics. The product from an emulsion polymerization is called ”latex” and a favorable atmosphere for environmentally friendly emulsion polymers have been a major driving force for rapid advancement of this technology. These water-based products have limitations in nature and it is not sure that they will achieve the excellent performance properties that are offered by solvent-based counterparts [8]. In the last years, the crude oil price has increased (110 U.S. dollars per barrel 23.05.11 [9]) and this makes it possible for the latex products to compete more effectively with solvent-borne polymer systems in other markets. The current trend may indicate that emulsion polymerization is an important field that deserves and needs more research and development resources. Emulsion polymerization has continued to attract attention of scientists since the first introduction of styrene-butadiene copolymers and polyvinyl acetate for latex paints around 1946-1950 [8].

Emulsion polymerization is a multiphase process, and polymerization proceeds as a double bond addition reaction that is initiated via a free-radical mechanism. Emulsion polymerization is therefore a conventional free radical polymerization and multiple different reactions will take place in the reactor. This process has primarily three liquid phases and reactions starts in the water phase. In water phase initiator decompose to free radicals and further combine with the dissolved monomer to form oligomers. These oligomers can get trapped by micelles and form particles, or the oligomers precipitate. Micelles are formed by excess surfactant that is utilized in emulsion polymerization. Polymerization reactions normally take place in the particle phase, and the rate of polymerization is not only controlled by monomer partitioning, but also by other phenomenas like particle nucleation, radical desorption and radical absorption. There has been a considerable progress in the fundamental understanding of emulsion polymerization mechanisms and kinetics after 1950. At present some key points such as particle nucleation and growth mechanisms and transport of free radicals with chemical reactions occurring in heterogeneous emulsion polymerization are still not completely understood. Colloidal stability and average number of radicals per particle is another task that is difficult to understand. All factors mentioned make modeling of emulsion polymerization difficult and challenging. Information of all this variables will require complex models and this often introduce several parameters with an unknown value.

A dynamic mathematical model should be fitted to measured data, and parameters have to be estimated off-line or on-line. It is not only different reaction phenomena that make the modeling difficult, but also numerical problems in solving sets of nonlinear ordinary differential equations, when the model is stiff and information on different model parameters lack.

As other processes, emulsion polymerization reactors are controlled with different control struc-tures implemented on the plant. Both new and older technology is utilized. There is a great potential for nonlinear model predictive control (NMPC) technology in the production of various types of polymer materials. Typical benefits are increased production rate or reduced batch time, less product quality variation, and better utilization of cooling capacity and raw materials. Model predictive control has become popular in chemical process industry due to its effective-ness in dealing with nonlinear multivariable and hard constraints. However, monitoring and control of polymerization reactors are a challenge due to lack of on-line sensors capable of monitoring the complex physic-chemical behavior within the system. To utilize NMPC on processes, a model that predict reasonable processes values are needed, and as modeling of emulsion polymerization is challenging, control with NMPC gets more difficult.

This work focuses on semi-batch emulsion polymerization processes, which are highly nonlinear and where the dynamics varies through the batch. To be able to utilize NMPC a nonlinear dynamic mathematical model has to be found and it is time-consuming and costly to develop mechanistic models suitable for use in NMPC applications. The objective of the thesis is to shorten the model development time, by defining a modular library of configurable sub-models. These sub-models will be tested on a case, which is emulsion polymerization of poly-vinyl chloride. To perform the modeling of an emulsion polymerization process some basic knowledge has to be understood. This work also has focus on the theory of emulsion polymerization and some theory will first be given. This theory is basic understanding needed to be able to model and control such processes.

1.2 Scope of work

The objective of this thesis is to make dynamic nonlinear control sub-models that can be utilized to model emulsion polymerization in semi-batch reactors. The work involves a wide range of assignments. This work has both a theoretical part, a modeling part that includes solving the model and estimating parameters and programming in MATLAB.

The work in this assignment consist of various tasks, and this are listed below.

- Give an overview of emulsion polymerization technology, with emphasis on topics influencing the dynamics and control of the reactors.
- Define a library of configurable sub-models, keeping in mind that;
  a. the library should be usable for a variety of industrial scale emulsion polymerizations
  b. the library should be easily expandable
  c. a model, built from the library, should be easy to adapt to several similar (but not identical) reactor configurations
  d. different products or product grades, with different recipes, may be produced in the same reactors
- Select a number of key sub-models from the definition above and formulate the corresponding model equations. Implement the sub-models in MATLAB.
- Decide which methods and tools that should be utilized for numerical integration of the models, keeping in mind that resulting models should be suitable for NMPC applications.
- Demonstrate the library utilize on a case study: Emulsion homo-polymerization of PVC. Configure models for this case. Fit model parameters to available process data.
- Based on the case study: Demonstrate model simplification techniques that help reduce computational load, while maintaining sufficient predictive accuracy.

Chapter 2

Fundamentals of Polymerization

This section gives an introduction of polymers and polymerization. Synthetic polymers have significant commercial importance and are known by several names, e.g. plastics, macromolecules and resins. These materials have become an important part of our daily existence, and efficient and economical production of polymers is important. Plastics are industrial goods used in e.g. building, construction, packaging, transportation, electronics, appliances, etc., industries.

2.1 Polymers

Polymers have been used for thousands of years, as there exist natural polymeric materials such as silk, wool and cotton. Biological materials such as DNA, proteins and mucopolysaccharides are also polymers [10]. Before the 1920's, chemists doubted the existence of molecules that had molecular weight greater than a few thousand [11]. Hermann Staudinger, a German chemist with experience in studying natural compounds, challenged this limited view of molecules and he proposed that these molecules were made up of macromolecules composed of 10.000 or more atoms [11]. A polymeric structure for rubber, based on repeating isoprene unit referred to as a monomer was formulated by Staudinger. In 1953 he received the Nobel Prize in Chemistry for his contributions to chemistry [11]. The names of polymer and monomer have Greek roots, where poly is many, mono is one and meros is part. The natural polymeric materials have been supplemented the last decades and the replaced materials are synthetic fibers such as nylon and acrylics. Polymers have been studied for many years and are still being studied among researches around the world. One important reason studying polymers is because of their behavior as materials are different from that of metals and other low-molecular weight molecules.

Polymers are materials with high molecular weight that are found to have many applications in our modern society. They are macromolecules. Polymers consist usually of multiple structural units (hundreds, thousands even tens of thousands), and these units are bounded together by covalent bonds. One example is polyethylene that is a long-chain polymer and is represented by a structural or repeated unit -CH_2-CH_2- and n represent the chain length of the polymer. Polymers are obtained through many chemical reactions of small molecular compounds called monomers. Polymeric materials are produced to have high strength, possess a glass transition temperature, exhibit rubber elasticity, and have high viscosity as melts and solutions [10].

These unique properties have made polymers extremely useful to mankind. These materials are used extensively in food packaging, clothing, home furnishing, transportation, medical devices, information technology, and so much more. There has been and still is considerable confusion concerning classification of polymers, and there are no single general accepted and unambiguous classification system for polymers [2]. Polymers can be classified according to one or more of the following criteria that is listed below [12]. It is important to know that these criterias are not unique and several other alternative classifications have been proposed in different literature.

- Chemical nature of monomers.
- Molecular structure of polymers.
- Polymer chain growth mechanism.
- Type of polymerization process.

2.1.1 Classification of polymers

Classifying polymers are based on their response towards heat, and there are two types of polymers; thermoplastics and thermosets. Another class of polymers is elastomers. Thermoplastics are linear and branched polymers that melt upon heating and solidify on cooling. The heating and cooling cycles can be performed several times, and this can be done without affecting the properties. When linear thermoplastics are melted they may pack in a regular three-dimensional arrangement, and a crystalline phase is formed upon cooling. Crystallization and the crystal size will depend on the type of monomer unit, rate of cooling, use of nucleating agents and chain architecture. The polymers have both a crystalline and amorphous regions because crystallization is never completed. This makes the polymers semi-crystalline. Crystalline regions are characterized by the melting temperature T_m, and the amorphous regions are characterized by the glass transition temperature T_g. Glass transition temperature is the temperature where amorphous polymers alter from hard objects to a soft rubbery state. Thermoplastics can be molded into different shapes, and constitute the vast majority of the polymers including polystyrene, poly (vinyl)chloride, polypropylene, etc. Thermosets are densely cross-linked polymers, and these melt only the first time they are heated. During the first heating the polymer is ”cured” and they do not melt when it is reheated, but is degraded. Elastomers are elastic materials and these stretch to high extensions and have the ability to recover their original dimensions once the applied stress is released. Elastomers are formed by a loose network. It is possible to make polymers that combine the characteristic of the thermoplastic and elastomers. These materials are A-B-A tri-block copolymers; composed by hard and soft segments. [13]

Polymers formed from a single monomer, therefore containing a single type of structural units are called homopolymers. The properties for the homopolymers are determined by the monomer used. If a range of properties are wanted, polymers formed by different monomers are performed and the ratio between the different monomers will determined the properties, and these are named copolymers.

Classification of polymers are also based on molecular structure, and three different structure are listed below [10].

1. Linear chain polymer.
2. Branched chain polymer.
3. Network or gel polymer.

In order to form polymers, monomers must have reactive functional groups, or double or triple bonds. Monomers functionality is defined to be the number of these functional groups. Double bonds are regarded as equivalent to a functionality of 2 and triple bonds has functionality of 4. Monomers have to be at least bifunctional to form a polymer, and when it is bifunctional the polymer chains are always linear. Thermoplastic polymers are linear molecules and in linear chains the repeated units are held together by strong covalent bonds. Different molecules are held together by secondary forces that are weaker than covalent bonds. If thermal energy is supplied to the polymer, the random motion will increase in the molecules, and this tries to overcome the secondary force. Molecules become free to move around and the polymer melts when all forces are overcome, and again this explains the thermoplastic nature of a polymer. Branched polymers consist of molecules having a linear backbone with branches emanating randomly from it. To form such a material the monomer has to be capable to grow in more than two directions. This means that the starting monomer must have functionality greater than 2. To form branched polymers of high molecular weight, special techniques have to be used. This will not be discussed, but if the reader is interested it is recommended to read Kumar and Gupta ([10]). If a polymer becomes a three-dimensional network it is called a gel. In fact, when a multi-functional monomer is polymerized, polymer evolves through a collection of linear chains to a collection of branched chains. This will form a network (or a gel) polymer. Network polymers do not melt upon heating and do not dissolve in solvents, like linear and branched polymers can do [13].

The synthesis of macromolecules composed of different monomeric repeating unit has been explored as a means of controlling the properties of the resulting material [11]. Two or more different repeated units can make up a chain-like structure, and it is known as a copolymer. There are several ways to incorporate different monomeric units in a polymeric molecule. A two component system is used to illustrate this, in which one monomer is designated A and the other B. First possible copolymer unit is statistical copolymers, also called random copolymers, and there monomeric units are distributed randomly and sometimes unevenly (-ABBAAABAABBBABAABA-). Second there is alternating copolymers, and here monomeric units are distributed in a regular alternating fashion, with nearly equimolar amounts of each in the chain (-ABABABABABABABAB-). Third there is block copolymers, and here long sequences or blocks of one monomer is joined to a block of the second monomer (-AAAAABB-BBBBBAAAAAAA-). The last one is graft copolymers, and these are formed when chains of one kind are attached to the backbone of a different polymer (-AAAAAAA(BBBBBBB-)AAAAAAA(BBBB-)AAA-).

A reaction mixture in a reactor, consist in practice of polymers made up of molecules with different molecular weight that vary over a range of values and are said to be polydisperse. In modeling an idealized sample of polymers are often used, and this consist of chains all having identical molecular weight. Such systems are called monodisperse polymers. The reader should know this, and not become confused when talking about monodisperse polymers, as this actually not exists.

2.1.2 Molecular weight distribution

Polymers contains chains of variable lengths and polymers are characterized by the molecular weight distribution (MWD). In polymerization, there are some techniques to determine MWD and its averages. The MWD affects the properties of the polymers and one example is the mechanical strength which is improved by increasing the molecular weight. MWD is often characterized by the average molecular weight given in Equation 2.1.1. In this Equation D_n and P_n are the number of moles of dead and growing polymer chains of degree of polymerization, n, that is the number of repeated units in the chain. [13]

$$\overline{M}_n = \frac{\sum n(D_n + P_n)}{\sum (D_n + P_n)} w_m \tag{2.1.1}$$

The weight average molecular weight is given in Equation 2.1.2. This is used to find the polydispersity index (PDI), which gives an idea about the broadness of the MWD. PDI is given in Equation 2.1.3.

$$\overline{M}_w = \frac{\sum n^2(D_n + P_n)}{\sum n(D_n + P_n)} w_m \tag{2.1.2}$$

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} \tag{2.1.3}$$

PDI will affect the properties applications. For a homopolymer, w_m is the molecular weight of the monomer, while for copolymer w_m is given in Equation 2.1.4, where F_{pi} is the molar copolymer composition referred to monomer i and w_i the molecular weight of this monomer [13].

$$w_m = \sum F_{pi} w_i \tag{2.1.4}$$

2.2 Polymerization

Small molecules that combine to each other to form polymer molecules are called monomers, and the reactions by which they combine are termed polymerization. Synthetic polymers can be produced from different reaction mechanisms and processes. There are different forms of polymerization and systems that categorize them. A major objective of polymerization reaction engineering is to understand how the reaction mechanism, the physical transport processes, reactor configuration and reactor operating conditions affect the macromolecular architecture (e.g. molar mass, molecular weight distribution (MWD), copolymer composition distribution, branching distribution) as well as morphological properties of the product (e.g. particle size distribution, porosity, etc.) [12].

2.2.1 Classes of polymerization

There are different classes of polymerization. There is chain-growth polymerization and step-growth polymerization. Step growth polymerization has reactive functional groups that are situated on each of the molecules and growth of polymer chains occur by reaction between these functional groups. As each molecule has at least one functional group, reaction can occur between any two molecules [10]. In chain-growth polymerization monomer polymerizes in the presence of compounds called initiators. Initiator used continually generates growth centers in the reaction mass, and this adds on monomer molecules rapidly. It is this sequential addition of monomer molecules to growing centers that make chain growth different from step growth polymerization [10]. There are several classes of chain-growth polymerization, and these are listed below [12]. As free-radical polymerization (FRP) and emulsion polymerization is of interest in this master thesis, this type of polymerization will be further explained.

- Coordination polymerization, where an active center is an active site of a catalyst.
- Free-radical polymerization, where active center is a radical.
- Anionic polymerization, where active center is an anion.
- Cationic polymerization, where active center is a cation.

Free-radical polymerization

Free-radical polymerization of vinyl monomers have carbon-carbon double bonds, and has been used in industry to make a variety of polymeric materials [8]. The active center is a free-radical in this type of polymerization. A free-radical is a reactive species that contain an unpaired electron, and the free-radical is created from an initiator. Free-radical polymerization has at least three basic reaction types that occur simultaneously during polymerization. The first is the initiation reaction which continuously makes radicals during polymerization. The second reaction is propagation that is responsible for the growth of polymer chains by monomer addition to a radical center. The last is bimolecular termination reaction between two radical centers which gives a net consumption of radicals. Generation of free-radicals can be from decomposition of azo and peroxide compounds, and this can be both thermally and by y-radication [12]. Chain polymerizations are extremely exothermic, and viscosity can increase rapid at relatively low conversions in bulk polymerizations. Monomer is consumed steadily throughout polymerization, and the reaction mixture contains monomer, polymer and growing polymer chains where the lifetime of a live polymer chain is of the order of 0.1-1 second [12]. This results in high molecular weight polymer formed from the beginning of the polymerization. In order to model radical polymerization kinetically, the different kinetic mechanisms have to be understood, and is therefore explained below.

Initiation

The homolytic decomposition of initiator molecules can be represented schematically as given in reaction 2.2.1. Homolytic decomposition of covalent bonds occurs with absorption of energy, which can be in form of heat, light or high energy radiation, depending on which initiator that is used [10].

$$I \xrightarrow{k_I} 2fI^{\bullet} \tag{2.2.1}$$

The primary radicals, $I^{\bullet}$, combine with a monomer molecule, M, according to the schematic reaction 2.2.2. In this reaction P_1 is the polymer chain radical having one monomeric unit.

$$I^{\bullet} + M \xrightarrow{k_i} P_1 \tag{2.2.2}$$

The effect of the reaction medium on the initiator can be found in different tables in chemical handbook, or other literature. In a polymerization process the initiator is inefficiently used. There is wastage of initiator due to normally two reactions. The first one induced decomposition of initiator, this happens by the attack of propagating radicals on the initiator. This reaction is called chain transfer to initiator. Induced decomposition of initiator does not alter the radical concentration during polymerization, as the newly formed radical will initiate a new polymer chain. A result from this reaction is wastage of initiator. A molecule of initiator is decomposed without an increase in the number of propagating radicals or the amount of monomer being converted to polymer. The second reaction, which will give wastage of initiator, is a reaction involving side reactions of the radicals formed in the primary step of initiator decomposition. Radicals formed in the primary decomposition step in the reaction, will undergo reactions that forms neutral molecules instead of initiating polymerization. When initiator efficiency is discussed, it is this last wastage reaction that it is referred to. Efficiency factor (f) is defined as the fraction of radicals formed in the primary step of initiator decomposition, which are successful in initiating polymerization. Another phenomenon that affects initiator efficiency should also be mentioned. This is the nature of the decomposition pathway that controls the efficiency of the primary radicals in initiating new polymer chains. This effect has been called the ”cage” theory. According to this theory the two dissociated fragments will be surrounded by reaction mass and this reaction mass will form a sort of cage around them. The two fragments will stay inside the cage for a finite amount of time, and within this time they may recombine to give back the initiator molecule. Fragments that not recombine will diffuse, and the separated fragments are called primary radicals. After primary radicals are formed, different reactions starts to occur. Primary radicals from different cage can recombine or react with monomer molecules to give P_1. [10]

Efficiency factor found in different literature should be used with care as initiator efficiency is considered exclusive of any initiator wastage by induced decomposition. This distinction is not always made in the literature values given. Calculations often neglect and do not correct for the occurrence of induced decomposition.

Propagation

Propagation reaction is defined as the addition of monomer molecules to the growing polymer radicals. Polymer radicals of all sizes are in the reaction mass. The propagation reaction is given in 2.2.3. P_n is notation for a polymer radical and there are n monomeric units joined together by covalent bonds in the chain radical. The rate constant for the reaction is denoted by k_p.

$$P_n + M \xrightarrow{k_p} P_{n+1} \tag{2.2.3}$$

Termination

Termination reaction is the reaction where polymer chain radicals are destroyed. Inactive polymer chains can be formed either by combination or by disproportionation. Termination by combination reaction are given in 2.2.4, and in this reaction two chain radicals combine to given an inactive chain. Termination by disproportionation reaction are given in 2.2.5, and in this reaction one chain radical gives up the electron to the other and both chains become inactive.

$$P_n + P_m \overset{k_{tc}}{\rightarrow} D_{n+m} \tag{2.2.4}$$

$$P_n + P_m \overset{k_{td}}{\rightarrow} D_n + D_m \tag{2.2.5}$$

In the equation given above I, $I^{\bullet}$, M, P_n, and D_n represent the initiator, initiator radical, monomer, free radicals with n monomeric units, and dead polymer chains with n monomeric units. The kinetic parameters k_I, k_i, k_p, k_{td} and k_{tc} are the thermal decomposition rate constant for the initiator, the initiator rate constant for the primary radical, the propagation rate constant for the reaction between one free radical with n monomeric units and one monomer molecule, the disproportional termination rate constant for the reaction between two free radicals, and the combination termination rate constant [8]. Polymerization proceeds by addition of monomer units to the active end of the growing polymer chain. The molecular weight of polymer builds up rapidly and grows to high weight molecules and in the end they terminates. After termination the high molecular weight polymer chain does not react further, and they are considered ”dead”. Dead chains have a residence time of minutes or hours in the reactor.

In some polymerization systems polymer molecular weight is observed to be lower than the predicted value. Chain stoppage (chain-breaking) can occur with a transfer mechanism. In this mechanism the growing radicals abstracts a weakly bonded atom, from monomer or other molecules in the system to generate a dead polymer chain as well as a new radical that initiates another polymer chain [13]. This weakly bonded atom is usually hydrogen, and other molecules can be monomer, polymer or chain-transfer agent (CTA). These radical displacement reactions are called chain transfer reactions, and the chain transfer of a propagating radical to monomer and polymer is given in 2.2.6 and 2.2.7. In these two reactions $k_{tr,mon}$ and $k_{tr,pol}$ are the rate constants for the chain transfer reaction of a propagating radical with monomer and polymer.

$$P_n + M \overset{k_{tr,mon}}{\rightarrow} P_n + P_1 \tag{2.2.6}$$

$$P_n + D_m \overset{k_{tr,pol}}{\rightarrow} D_n + P_m \tag{2.2.7}$$

The effect of chain transfer on the polymerization rate depend on whether the rate of reinitiation is comparable to that of the original propagating radical [2]. Chain transfer is an important phenomenon, as it can alter the molecular weight of the polymer product in an undesirable manner. Controlled chain transfer may be employed to advantage in the control of molecular weight at a specified level. If it is assumed that small radical species are not consumed by side reactions and do not accumulate in the system, but instead are converted to polymeric radicals (close to 100% efficiency), a set of rate laws can be formulated. These are listed below [13].

- Initiator decomposition: $R_I = k_I[I]$
- Chain initiation: $R_{ini} = 2fk_I[I]$
- Chain propagation: $R_{prop} = k_p[M][P_{tot}]$
- Chain termination: $R_{term} = (k_{tc} + k_{td})[P_{tot}]^2 = k_t[P_{tot}]^2$
- Chain transfer: $R_{tr} = (k_{tr}^{mon}[M] + k_{tr}^{pol}[P] + k_{tr}^{CTA}[CTA])[P_{tot}]$

In the rate laws given $[P_{tot}]$ is the concentration of all polymer radicals in the system. Polymerization rate can be measured experimental, but then it is not possible to resolve the quantities into estimates of individual rate coefficients [13]. Both efficiency (f) and the rate constant (k$_I$) have to be known, and an assumption usually made is that radicals are not being consumed or trapped by impurities in the system. These factors have led to broadness of the coefficients reported in the literature. Individual values of the rate constants and how they vary with temperature are required for model development and an accurate representation of multi-monomer system. Different experimental techniques have been used to find information that can be used to calculate the rate constants, especially for propagation, initiation and termination.

Chapter 3

Emulsion polymerization

Emulsion polymerization is a widely used process for the production of different synthetic latex products with a variety of colloidal and physiochemical properties [8]. This process was first commercialized in the early 1930s, and today millions of tons of synthetic polymer latex are prepared by using emulsion polymerization. It should be mentioned that latex is the name for the final product of an emulsion polymerization process, and is often used directly for an emulsion where separation of the polymer from the water and other components have not been performed. A variety of synthetic polymers are produced and this includes synthetic elastomer, bulk plastics and plastic/elastomeric lattices for coatings. Main products and markets are paints and coatings, paper coating, adhesives and carpet backing. Another interesting market is biomedical applications, for diagnosis, drug delivery and treatment [13]. The major developments in emulsion polymerization started around the Second World War, where this was a result of the intensive collaborative efforts between academia, industry and government laboratories [14].

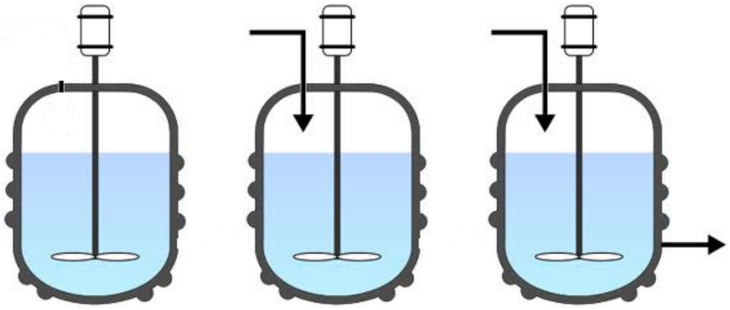
Emulsion polymerization is a heterogeneous free radical polymerization process. It involves the polymerization of monomers that are in the form of emulsion. This is a complex process because nucleation, growth and stabilization of polymer particles are controlled by the free radical polymerization mechanisms, in combination with other colloidal phenomena. The main components in emulsion polymerization are monomer(s), dispersant, emulsifier (surfactant), and water-soluble initiator. The dispersant is the liquid, usually water, in which the various components are dispersed in an emulsion state by means of emulsifier [2]. Emulsion polymerization involves emulsification of relatively hydrophobic monomers in water by an oil-water emulsifier, followed by initiation reaction with either a water-insoluble initiator or an oil-soluble initiator [15]. There are a large number of different monomers that can be used in emulsion polymerization, i.e. butadiene, styrene and vinyl chloride. As particle nuclei form and grow in size with the progress of the polymerization, a large oil-water interfacial area will be generated. The emulsifier will start to stabilize, as this molecule will both physically be adsorbed or chemically incorporated into the particle surface so that interactions between latex particles are prevented.

There are some main issues in dealing with the kinetic and mechanisms of emulsion polymerization. This involves the understanding of the process by which latex particles form and grow. This include information about the particle size or particle number and size distribution, development of molar mass and molar mass distribution, polymerization rate profile, and how polymerization rate are influenced by the basic polymerization parameters such as surfactant type, initiator type, monomer, temperature and rate of monomer addition. Emulsion polymerization is a free-radical polymerization and all the kinetic events like initiation, propagation, termination and transfer reaction are applicable to describe the overall rate of the polymerization and molar mass developments [14]. The problem is the heterogeneous nature of the polymerization that creates complications due to partitioning of the various molecules between the phases. In emulsion polymerization there is a micellar phase, aqueous phase, monomer droplet phase and a particle phase (polymer-rich phase). To get acceptable information about all this in the process, a good model of the process is required and this model should be readily to solve.

There exist a large variety of literature concerning emulsion polymerization, some aspects of this technology will be covered in this thesis.

3.1 Reactors used for emulsion polymerization

To produce latex products there are normally three types of reactors that can be used. This is batch reactor, semi-batch reactor and continuous reactor (see Figure 3.1). They will all be briefly discussed, and the main focus further is semi-batch reactor.



(a) Batch reactor **(b)** Semi-batch reactor **(c)** Continuous reactor

Figure 3.1: Three types of reactors commonly used to produce latex products

Few latex products are manufactured in large-scale batch polymerization systems. Batch emulsion polymerization is generally used in the laboratory to study reaction mechanisms, develop new latex products and to obtain kinetic data for process development and reactor scale-up. As free-radical polymerization is highly exothermic in nature there will be several problems in controlling the reaction temperature in a batch reactor, compared to the two other possible reactors. The heat-transfer capacity is limited due to the small surface-to-volume ratio of large-scale batch reactors. The two most used reactor types are continuous and semi-batch reactors. An important difference among the three polymerization processes is the residence time distribution [1] (RTD) of the growing particles within the reactor. The broadness of residence

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[1] Residence time distribution (RTD) of a chemical reactor is a probability distribution function that describes

time distribution in decreasing order is single continuous > semi-batch > batch. This results in the broadness of the resultant particle size distribution in decreasing order is single continuous > semi-batch > batch. Continuous reactors include the plug-flow reactor (PFR), and this behaves much like the batch reactor in terms of RTD, if the length of the PFR is long enough. There are observed different fluid dynamics pattern in the PFR and batch reactors, and this have an influence on the properties of latex products. The rate of polymerization follows the trend: batch > semi-batch > continuous. [8]

The continuous and semi-batch emulsion polymerization systems are both versatile and can offer flexibility to prepare latex products with controlled particle size distribution, polymer composition, and particle morphology. This serves as an effective tool to design specialty emulsion polymers those exhibit performance properties that the customers require. [8]

3.2 Description of process

Emulsion polymerization formulations typically comprise monomer, water, emulsifier and a water-soluble initiator. The monomer used is dispersed in water in the presence of emulsifier. An emulsifier, also called emulgent, is a substance which stabilizes an emulsion by increasing its kinetic stability. Emulsifiers are known as surface active substances, or surfactants, and are typically used to keep an emulsion (mixture of immiscible fluids) well dispersed. Surfactants usually have a hydrophobic and a hydrophilic end. The surfactant will surround the immiscible molecule and form a protective layer so that molecules in the reactor do not ”clump” together. This keeps the dispersed phase in small droplets and preserves the emulsion. Surfactants are usually organic compounds and these are amphiphilic. The surfactant will adsorb on the surface of the monomer droplets and stabilize them. The emulsified monomer droplets characterizes the reaction system, and these monomer droplets are approximately 1-10 μm in diameter. If the concentration of a surfactant exceeds its critical micelle concentration (CMC), excess surfactant molecules will aggregate together to form small colloidal clusters referred to as micelles. The transformation of a solution to the colloidal state as the surfactant concentration exceeds the CMC occurs to minimize the free energy of solution. This is accompanied by a rapid drop in the surface tension of the solution. In emulsion polymerization the surfactant concentration can exceed CMC by 1-3 orders of magnitude, so the bulk of the surfactant is inside the micelles. Each micelle contains about 50-150 surfactant molecules and the shape of the micelle depends on surfactant concentration. Water-insoluble initiator and only slightly soluble monomer is added to the reaction mixture, and a small fraction of monomers will dissolve and go into the solution. Water solubility of common monomers used in emulsion polymerization are quite low, e.g. styrene, butadiene, vinyl chloride and vinyl acetate are soluble to the extent of respectively 0,07, 0,8, 7 and 25 g/liter at room temperature. The largest portion of the monomer is dispersed as monomer droplets; the size of these monomer reservoirs depends on the intensity of agitation. [2]

Initiator is present in the water phase and the initiating radical's starts to be produced. The rate of radical production is typically of the order of 10^{13} radicals per milliliter per seconds, and the locus of polymerization is now of prime concern. As most initiator used is water-

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the amount of time a fluid element could spend inside the reactor soluble, radicals are formed in the aqueous phase. An oil-insoluble initiator is used, and this is what makes emulsion different from suspension polymerization, as in suspension oil-soluble initiator is normal to use. Site of polymerization is not the monomer droplets, as the radicals formed are to hydrophilic to directly enter into the organic monomer [13]. In suspension the reaction will occur in the monomer droplets [2]. As the micelles exhibit a large oil-water interfacial area, the monomer droplets are not effective in competing with micelles in capturing free radicals generated in the aqueous phase due to their relatively small surface area. The mechanism for particle nucleation, formation of polymer particles, is described by two simultaneous processes in emulsion polymerization. The first is entry of radicals from the aqueous phase into the micelles, called micelle nucleation. The other, is homogeneous nucleation that involves solution-polymerized oligomer radicals that becomes insoluble and precipitating on themselves [2].

To get an overview of a emulsion polymerization system, see Figure 3.2. As can be seen from this figure the system consist of three types of particles; active micelles in which polymerization occur, inactive micelles in which polymerization do not occur and monomer droplets. Active micelles are no longer considered as micelles but are referred to as polymer particles.

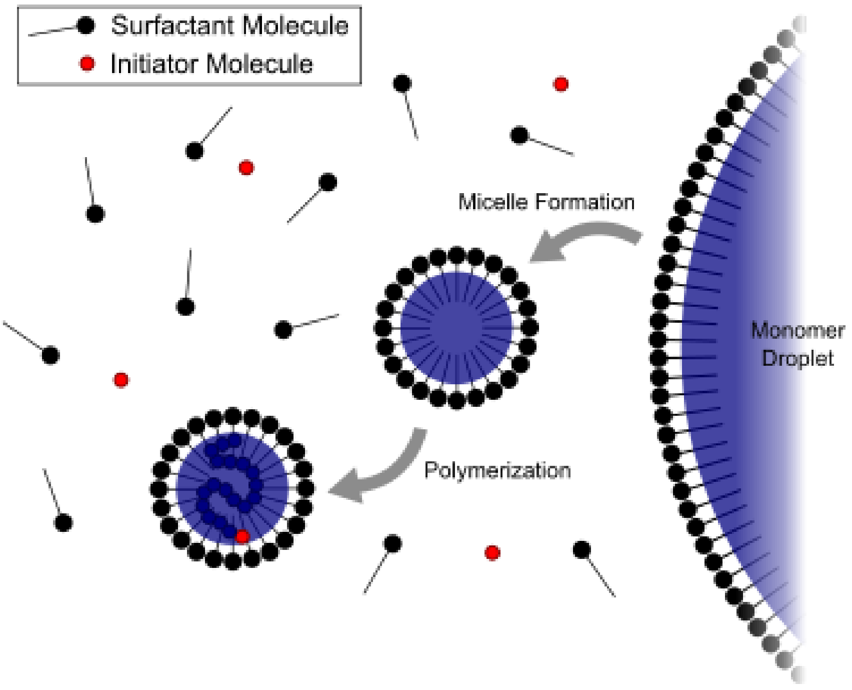


Figure 3.2: Simplified representation of an emulsion polymerization system [1].

Elementary chemical reactions will be given for a general emulsion polymerization process, even though in a real reactor more reactions will occur. To make a model that is acceptable for control purpose and give a readily overview of an emulsion polymerization process, the most important reactions have to be considered. Reactions utilized further in this work are listed below. Most of these reaction have been explained already in Section 2.2.1.

Initiator decomposition:

$I \xrightarrow{k_I} 2fI^{\bullet}$

Chain initiation:

$I^{\bullet} + M \xrightarrow{k_i} P_1$

Chain propagation:

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

Chain termination, first by combination and second by disproportionation:

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

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

Chain transfer to monomer:

$$\begin{aligned} &P_n + M \xrightarrow{k_{tr,mon}} D_n + M^{\bullet} \\ &M^{\bullet} + M \xrightarrow{k_{i,mon}} P_1 \end{aligned}$$

Chain transfer to CTA:

$$\begin{aligned} &P_n + CTA \xrightarrow{k_{tr,CTA}} D_n + CTA^{\bullet} \\ &CTA^{\bullet} + M \xrightarrow{k_{i,CTA}} P_1 \end{aligned}$$

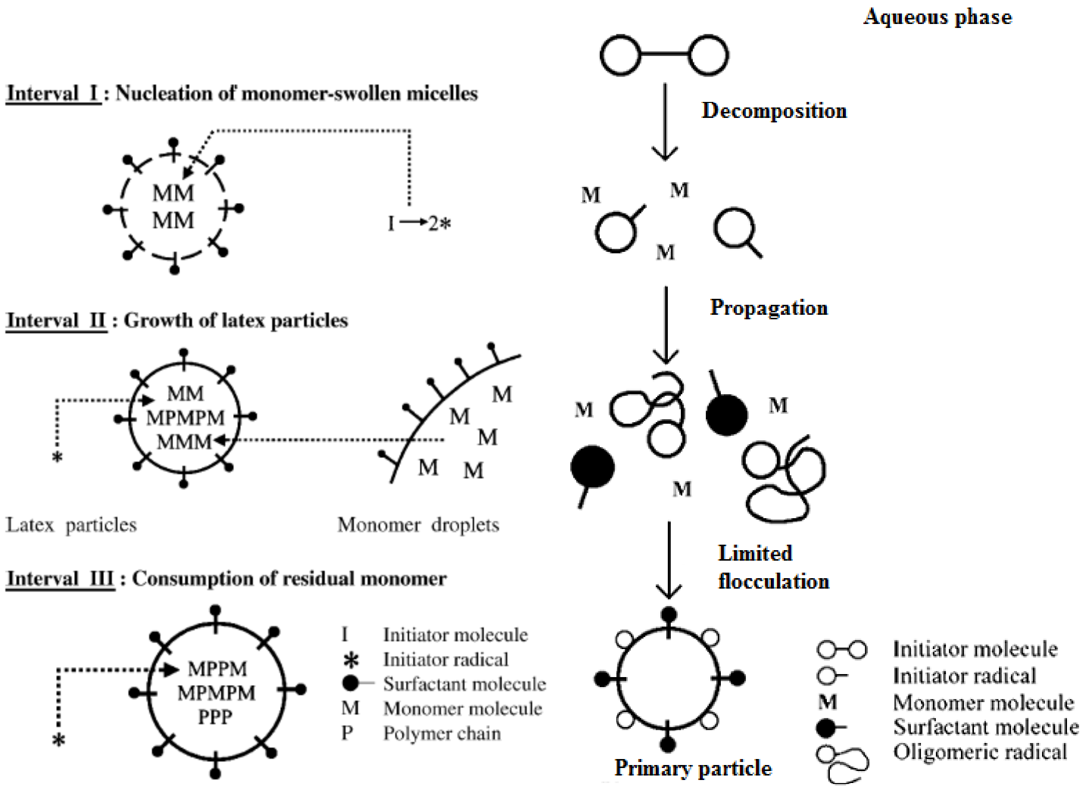
Chain transfer to polymer:

$P_n + D_m \xrightarrow{k_{tr,pol}} D_n + P_m$

The main advantages of the emulsion polymerization are; low viscosity of the reaction mixture, readily thermal control of the reactor, virtually 100% conversion can be achieved, high polymerization rate, final latex may be directly usable. Its disadvantages are; emulsifier and coagulants are hard to remove from the final polymer (e.g. high residual impurity), the production cost is higher than that of suspension systems [12]. One of the most striking features of emulsion polymerization is the segregation of free radicals among the discrete monomer-swollen polymer particles. This reduces the probability of bimolecular termination of free radicals and this results in a faster polymerization rate and polymer with a high molecular weight [15]. This cannot be achieved simultaneously in bulk or solution polymerization, so it is an advantageous characteristic of emulsion polymerization.

3.2.1 Miceller nucleation and homogeneous nucleation

Free radicals polymerize first with monomer molecules that are dissolved in the continuous aqueous phase. This results in increased hydrophobicity of oligomer radicals, and when a critical chain length is achieved these radicals are so hydrophobic that they have a tendency to enter the monomer-swollen micelles [15]. In the monomer-swollen micelles they continue to propagate by reacting with those monomer molecules therein. This is called micellar nucleation. Monomer-swollen micelles are thereafter transformed into particle nuclei, and these embryo particles continue to grow [15]. Adequate colloidal stability is important to maintain the growing particle nuclei, and micelles that do not contribute to particle nucleation disband to supply the increasing demand for surfactant. Surfactant molecules that are on the monomer droplets may desorb and diffuse across continuous aqueous phase and then adsorb on the expanding particle surface [15]. Surfactant concentration is an important parameter that controls the particle nucleation process. This is given from the Smith-Ewart theory. This theory indicates the important relationship that the particle number depends on the 0,6 power of the emulsifier concentration and on the 0,4 power of the initiator concentration [16]. Figure 3.3a shows a simple representation of the micelle nucleation model.



(a) Micellar nucleation model [15] **(b)** Homogeneous nucleation mechanism [8]

Figure 3.3: A schematic representation of nucleation

Homogeneous nucleation mechanism is when formation of particle nuclei happen in the continuous aqueous phase [8]. This is illustrated in Figure 3.3b. Waterborne initiator is first generated by the thermal decomposition of initiator and they grow in size because of the propagation reaction with monomer molecules dissolved in the aqueous phase. The oligomer radicals become water-insoluble when a critical chain length is reached [15]. Hydrophobic oligomer radicals may coil up and form a particle nucleus in the aqueous phase. After this, formation of a stable primary radicals occur via the limited flocculation of the relatively unstable particle nuclei and adsorption of surfactant molecules on their particle surfaces [15]. Surfactant that is needed to stabilize these primary radicals comes from those that have dissolved in the aqueous phase and those that have adsorbed on the monomer droplet surface. Particle nucleation from the different mechanisms controls the particle size and particle size distribution of latex products.

Extents of micellar and homogeneous nucleation will vary with the water solubility of the monomer and the surfactant concentration. Higher water solubility and low surfactant concentration will favor the homogeneous nucleation. Micellar nucleation is therefore favored by low water solubility and high surfactant concentration. [13]

3.3 Progress of emulsion polymerization

Polymerization rate versus conversion has been observed to have several distinct behaviors depending on the rate of initiation, propagation and termination. This also depends upon monomer and reaction condition in the process. This is shown in Figure 3.4 which shows three intervals with different behaviors.

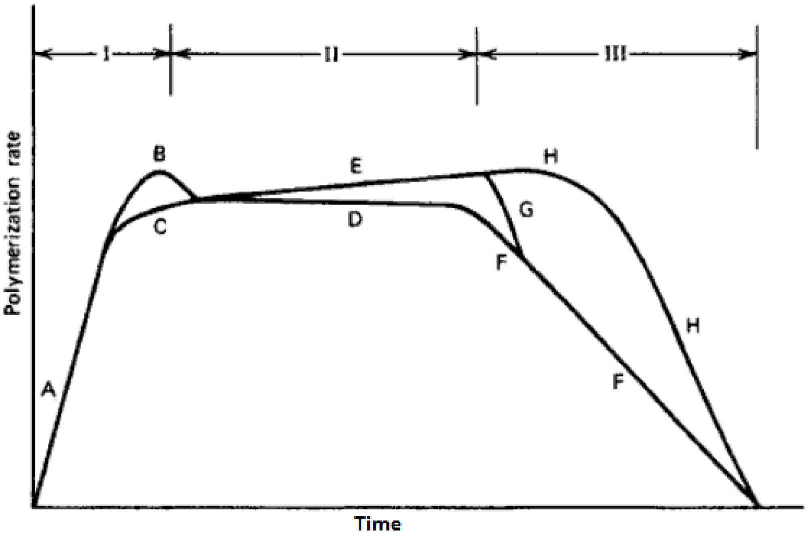


Figure 3.4: Different rate behaviors observed in emulsion polymerization. [2]

Emulsion polymerization process can be divided into three intervals (I, II, III) based on particle number and existence of a separate monomer phase (See Figure 3.4). There will be a separated monomer phase in Interval I and II, but not in Interval III. Polymer particles are generated and particle number increase in Interval I with time, but remains constant in the two last intervals.

Particle nucleation occurs in Interval I and polymerization rate increase with time as the particle number builds up. Monomers diffuse into the polymer particles and replace monomer that has reacted, and these monomers come from the separate monomer phase that is called a monomer reservoir. The system undergoes a significant alteration in Interval I, where the particle number stabilizes at a value which is a small fraction. This value is about 0,1 % of the concentration of micelles initially present. Polymer particles grow in size and contain both polymer and monomer, and they absorb more surfactant from the solution as they grow, to maintain stability. A point is reached when surfactant concentration falls below its CMC, and then inactive micelles become unstable and disappear with dissolution of micellar surfactant. In end of Interval I or early in Interval II all, or almost all, of the surfactant in the system has been absorbed by the polymer particles. As all the surfactant is absorbed on the polymer particles the monomer droplets starts to get unstable and will coalesce if agitation is stopped. Interval I is the shortest of the three intervals and its duration vary in the range 2-15% conversion. For low initiation rates, Interval I is longer, as more time is needed to attain the steady-state particle number. More water soluble monomers tend to complete Interval I faster than less water-soluble monomers. In Figure 3.4 the predicted maximum (curve A-C) comes from a transient high particle number and/or high proportion of particles containing propagating radicals. This maximum is often only observed for some monomers when initiation rates are high. [2]

Monomer concentration in the particles is maintained at saturation level by diffusion of monomers from the solution in Interval II. This is the reason for polymerization proceeds in the polymer particles. This is again maintained at saturation level by dissolution of monomers from the monomer droplets. Monomer concentration in polymer particles is high, and the volume fraction of monomer depends on which monomer used in the process, i.e. volume fraction of monomer is 0,3 for vinyl chloride. The polymerization rate can be either constant (D) or increase slightly with time (E) during Interval II. Transition from Interval II to III occurs at lower conversions as water solubility of monomer increases and the extent of swelling of polymer particles by monomer increases. In Interval III particle number remains the same, but monomer concentration in the polymer particles decrease with time as monomer droplets are no longer present. Polymerization rate in Interval II cannot be maintained in Interval III, so it decreases. Something that is worth to mention is that polymerization rate can increase rapidly with increasing monomer conversion. This is because of the reduced bimolecular termination reaction between two polymeric radicals within the viscous particle. This is provided that polymerization is performed at a temperature below the glass transition temperature of the monomer-starved polymer solution. This phenomenon is called the gel effect and presence of this gel effect continuous in Interval III. Polymerization continues at a steadily decreasing rate as monomer concentration in the polymer particles decrease. In production of polymers hazards to end-users in the product have to be avoided and residual monomer in latex products have to be minimized. [2]

3.3.1 Gel effect

The gel effect is a phenomenon that often take place in free radical polymerization process at intermediate or high degrees of conversion. The gel effect is a sudden increase of the rate of a free radical polymerization, and an increase in the viscosity of the reacting medium. This is caused by diffusion limitations that slow down the termination, but not the propagation reaction.

Free radical polymerizations are highly exothermic, and a sudden increase of the temperature may result in a reaction runaway, lower the quality of end product and induce instabilities in the process. It is therefore important to be able to predict and possibly reduce the gel effect. This effect has not been considered further, and is therefore not modeled in the later part of this thesis. [17]

3.4 Mechanisms, kinetics and thermodynamic

In emulsion polymerization most of the polymerization occur in the polymer particles. Radicals that are formed in the aqueous phase from water-soluble initiator, react with monomers that are dissolved in the aqueous phase forming oligoradicals [13]. These oligoradicals may;

1. enter the polymer particles.
2. enter into the micelles and a heterogeneous nucleation occur.
3. radicals can propagate in the aqueous phase until they become insoluble and precipitate forming a new polymer particle. This is a homogeneous nucleation.
4. they can terminate with other radicals in the aqueous phase.

Each of the events listed above may happen, but they depends on the particular conditions of the system. Some of these conditions are emulsifier concentration, number of polymer particles, initiator concentration, monomer type, etc. In the polymer particle, polymerization follows the same mechanisms as in bulk-free radical polymerization [13]. These mechanisms involve chain transfer to small molecules, e.g. monomers and CTA, and this yield small radical. These small radicals can exit the polymer particle and diffuse out to the aqueous phase. The transfer reactions can occur anywhere on the polymer chain [10]. There are large amounts of reaction that actually occur in emulsion polymerization, but the most important ones are considered. These reactions are already given in Section 3.2.

3.4.1 Radical compartmentalization

Radicals are distributed among the polymer particles, in an emulsion polymerization system. There are few radicals per particle because of the small size of the particles. Compartmentalization of radicals among particles is the most distinctive kinetic feature of emulsion polymerization and has an influence in both polymerization rate and polymer micro structure. The overall radical concentration in emulsion polymerization is greater than in bulk polymerization because the radicals in different particles cannot terminate by bimolecular termination. This will further give a higher polymerization rate in emulsion polymerization than in bulk polymerization. The radical concentration in the reactor will increase as the number of particles increase. A longer life-time of the radicals, which leads to higher molecular weight, is also a result of the radical compartmentalization. For systems described here, the polymer chains will grow until a second radical enters the particle, and terminates. Because of this, the chain length is inversely proportional to the entry frequency. With a given initiator concentration frequency of radical entry decreases with the number of particles, and therefore increases the molecular weight. It is therefore possible in emulsion polymerization to simultaneously increase the polymerization rate and the molecular weight by increasing the number of particles. [13]

Transport of free radicals between the particles and continuous aqueous phase determines average number of free radicals per particle during polymerization. Radicals generated in the aqueous phase can be absorbed by particles in Interval II. Desorption of radicals out of particles, may also occur in polymerization, and this process begin with a chain transfer reaction of a polymeric radical. Radicals that have desorbed have a chance to be absorbed again by another particle and reinitiate the propagation reaction therein. [15]

3.4.2 Polymerization rate

The rate of polymerization (rate of reaction) in emulsion polymerization is given in Equation 3.4.1. In this Equation k_p is the rate constant for propagation, $[M]_p$, is monomer concentration in the polymer particles, N_p is total number of particles in the reaction mixture per liter of water, $\bar{n}$ is average number of radicals per polymer particle and N_A is Avogadro's number. Which unit N_p has will influence other equations, and N_p can be given as number of particles or moles of particles in the reactor without dividing this on water volume. [13]

$$R_p = \frac{k_p [M]_p N_p \bar{n}}{N_A} \tag{3.4.1}$$

In Equation 3.4.1, $\frac{N_p \bar{n}}{N_A}$ is the concentration of radicals in the polymer particle. The prediction of particle number and size is not readily to accomplish and there are several reasons for this. One reason is the measurement of number and size of polymer particles which are in the region of a few hundred angstroms presents extremely difficult experimental problems [2].

According to the Smith-Ewart scheme that are well known and often used, R_p in Interval I increase due to the increasing number of particles that are newly formed. In Interval II R_p will remain relatively constant, as no new particles are formed and the monomer concentration inside the particles $[M]_p$ is almost constant based on thermodynamic equilibrium. It is important to notice that the Smith-Ewart equation is most successfully applied to monomers with very low water solubility, e.g. styrene. Monomers with higher water solubility deviate from the Smith-Ewart classical kinetic scheme for different reasons. One reason is that if the monomer is water soluble, there will be additional water phase polymerization. Another reason is that if there is significant radical desorption present, the average number of radicals per particle will be lower than 0,5. If this is lower than 0,5 the response of rate of polymerization to alterations in emulsifier concentration will not be predicted by Smith-Ewart theory. [18]

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[2] Angstrom is a unit of length used to measure small things such as the wavelengths of light, atoms and molecules. Ten billion angstroms equal 1 meter. The symbol is Å.

3.4.3 Average number of radicals per particle

The value of average number of radicals per particle during the batch is of critical importance in determining the rate of polymerization, and has been subject of much theoretical and experimental work. There are three cases normally used in literature and this is based on the work of Smith and Ewart, and others. The difference between these three cases are the occurrence of radical diffusion out of the polymer particles, particle size, modes of termination, and the rate of initiation and termination process relative to each other [2].

Case 1: $\overline{n}$ < 0,5

If $\overline{n} < 0{,}5$ than most of the polymer particles contain zero or one radical. The average number of radicals per particle drop below 0,5 if the rate of radical desorption from particles are rapid. In systems where radical desorption rate is faster than the rate of entry the average number of radicals per polymer particle can get smaller than 0.5. The decrease in average number of radicals per particle is larger for small particle sizes and low initiation rates. [2].

Case 2: $\overline{n}$ = 0,5

Case 2 occur when desorption of radicals does not occur or is negligible compared to the rate of radicals entering particles, also called absorption of particles. It will also occur if particle size is too small, relative to the bimolecular termination rate constant, to accommodate more than one radical. In this case a radical that enters a particle will be trapped within the particle and undergoes propagation until another radical enters the particle. When this happens, an instantaneous termination will occur. A particle will be active half of the time, and dormant the other half. At any given time, half of the polymer particles contain zero radical and the other half has one radical and is growing. The number of radicals per particle averaged over all particles is 0,5. In this case termination in the water phase is neglected, and the initiation rate is not too low. [2]

Case 3: $\overline{n}$ > 0,5

Some of the polymer particles have to contain two or more radicals per particle, in order for $\overline{n}$ to be larger than 0,5. There will also always be a fraction in the reactor that contain zero radical per particle. In order to have $\overline{n} > 0{,}5$ the particle size has to be large or the termination rate constant is low. In this case termination in the aqueous phase and desorption are not important. [2]

In most literature found, case 2 shows to be the dominant behavior for all monomers, but this is actually not true. Vinyl acetate and vinyl chloride are both following case 1 behavior under a variety of reaction conditions. Average number of radicals per particle is observed to be approximately 0,1 or lower for vinyl acetate and vinyl chloride. Monomers that show strong case 1 behavior are those with high monomer chain transfer constants. Case 3 behavior occurs when particle size is large relative to the termination rate constant (k_t), such that two or more radicals can coexist in a polymer particle without instantaneous termination. [2]

Calculating average number of radicals per particle

Average number of radicals per particle can be obtained by performing balances on the number of particles, *N(j)*, containing *j* radicals at any instant [19]. After balances on the number of particles are given, the average number of radicals per particle can readily be found with Equation 3.4.2. This number depends on relative rate of entry, exit and termination of radicals.

$$\overline{n} = \frac{\sum_{j=0}^{j_{\max}} jN(j)}{\sum_{j=0}^{j_{\max}} N(j)} \tag{3.4.2}$$

Expressions utilized to derive the balance on the number of particles, *N(j)*, contain parameters that are difficult to estimate, and are influenced by the mechanistic assumptions used in their derivation. The rate of radical termination in the polymer particle with n radicals is given in Equation 3.4.3 as R_T. In this equation k_t is the termination rate constant, v_p is the volume of a monomer swollen polymer particle.

$$R_t = \frac{k_t}{v_p N_A} j(j-1) \tag{3.4.3}$$

Radical exit will also occur in particles, and this will also depend on which process that are considered. Exit occur by chain transfer to a small molecule followed by diffusion of the small radical to the aqueous phase. The rate of radical desorption from a particle with n radicals is given in Equation 3.4.4. In this equation k_{de} is the desorption rate coefficient from particles containing n radicals. This rate coefficient is not readily to find, as it depend on the number of radicals per particle. The is simplified by using an average value for k_{de}.

$$R_{exit} = k_{de(j)} j \tag{3.4.4}$$

In emulsion polymerization, radical desorption is one of the most important physical processes influencing the kinetics. For desorption to occur from any polymer particle, the molecule has to reach the particle surface during random diffusion through the polymer phase. The molecule has to survive different possible competitive reactions that take place simultaneously in the particle. When it is on the surface it must also overcome a certain energy barrier in order to leave the particle. This energy barrier can be determined by the difference in the chemical potential of the molecule between the particle and the continuous phase. [20]

The final population balance is given in Equation 3.4.5, and from this equation it can be seen that moles of radicals in water have to be known. Units used in this balance can be both number and moles of polymer particles with *j* radicals, dependent on *N(j)* is given as number of particles with *j* radicals or moles of particles with *j* radicals. The first term is entry in $N_{(j-1)}$, second term is desorption from $N_{(j+1)}$, third term is termination in $\mathrm{N}_{(j+2)}$, fourth term is entry in $N_{(j)}$, fifth term is exit from $N_{(j)}$ and the last term is termination in $N_{(j)}$, and j=0,1,2,3.... (Moles/s). Inhibitor can be utilized in some process, and this is consumed through reactions with radicals.

Its reactivity is supposed to be independent of the nature of the radicals.

$$\begin{aligned}&\tfrac{dN(j)}{dt} = k_a N_{rw} N_A N_{(j-1)} + k_{des}(j+1)N_{(j+1)} + \tfrac{k_t}{v_p N_A}(j+1)(j+2)N_{(j+2)} - k_a N_{rw} N_A N_{(j)} \\ &-k_{des} j N_j - \tfrac{k_t}{v_p N_A} j(j-1)N_j + k_{zp}(j+1)N_{(j+1)} - k_{zp} j N_j\end{aligned} \tag{3.4.5}$$

3.4.4 Number of particles

Nucleation stage constitutes the so-called Interval I, and this is the initial period in which the particle number is changing. Nucleation of new particles can also take place during Interval II and III, and this is often referred to as secondary nucleation. This is often encountered in systems with poor stability or with changing composition. All discussions of particle nucleation start with Smith-Ewart theory, where they managed to obtain an equation for the particle number as a function of surfactant concentration and initiation and polymerization rate. Other scientists have argued against the Smith-Ewart theory, as the equation is developed mainly for systems of monomer with low water solubility. Another reason is that particles can be formed without micelles in the mixture. [18]

Radicals are absorbed into monomer-swollen emulsifier micelles in emulsion polymerization, and these are then transformed into polymer particles. Rate of radical absorption is equal to the rate of initiator decomposition and this is given in Equation 3.4.6. [18]

$$\frac{dN_p}{dt} = \rho_i = 2fk_I N_{ini} N_A \tag{3.4.6}$$

Avogadro's number is utilized to make the units correct, as N_p is the particle number. If N_p is given in moles, Avogadro's constant is not necessary. The surfactant will start to adsorb on particles formed, but if the surfactant concentration is above the CMC, micelles are created. This is usual for emulsion polymerization, and as mentioned monomer swollen emulsifier micelles are created. Number of micelles will decrease as the particles grow, giving an increasing surface which will adsorb surfactant. Particle formation stops when all surfactant is adsorbed on the particles. As all surfactant is adsorbed on the particle the total particle surface (A_p) is equal to the total surface area of surfactant ($a_s S$), where a_s is the specific surface area for the surfactant and S the amount of surfactant (i.e. mole).). To be precise then actually S is the amount in excess of the critical micelle concentration. The difference is not that important if CMC is significant lower than amount of surfactant, something that often occur as CMC is low for a surfactant. Some of the polymer particles will also absorb radicals, and this is leading to a decrease in the rate of nucleation and again a lower number of particles. For computational purposes the rate of radical absorption is set proportional to the particle surface area $A_p = \sum a_p$. From this a new equation for the particle number is found (Equation 3.4.7).

$$\frac{dN_p}{dt} = \rho_i\left(1 - \frac{A_p}{a_s S}\right) = \rho_i\left(1 - \frac{N_p a_p}{a_s S}\right) \tag{3.4.7}$$

It would be most correct to find how the particles grow, and use a_p as a state ($\frac{da_p}{dt}$). An expression for A_p has to be found, as the surface will increase with time. Another method to calculate numbers of particles are by using Harkins Smith-Ewart theory, and the equation they found for an upper and lower limit.

Harkins Smith-Ewart theory

This theory is based on Harkin's micellar theory and assumes that the free radicals generated by initiator in the aqueous phase are absorbed in monomer swollen micelles [21]. As the particles grow at a constant rate during the nucleation period, the number of particles nucleated is not proportional to the number of micelles. Rate of absorption of radicals is either assumed constant, an upper limit, or decreasing with time because of competition from the new particles formed, a lower limit [21]. These two limits produce the same dependence on emulsifier and initiator concentration, but they will differ with a numerical factor. Expression used to find the number of particles formed is given in Equation 3.4.8. The derivation of this is given in different literature, i.e. [8] and [22].

$$N_p = kN_A(\rho_i/\mu)^{2/5}(a_sS)^{3/5} \tag{3.4.8}$$

In Equation 3.4.8 ρ_i is the rate of radical generation, $\mu = dv/dt$ is the rate of particle volume growth, a_s is the specific area of the surfactant and S is the surfactant concentration. A problem using Equation 3.4.8 is that $\mu = dv/dt$ is not readily to find. The upper and lower limits given by Smith and Ewart differ only by the constant k. This constant is between 0,53 (upper limit) and 0,37 (lower limit) [21]. The upper limit implies that only micelles can absorb free radicals, and the lower limit is calculated on the basis that both particles and micelles absorb radicals at a rate proportional to the surface area [22]. In different literature the radical absorption rate is proportional to the particle radius and not to the surface as assumed in the Smith-Ewart theory. Because of this the value of k is expected to be between the two limits [21]. The drawback with Smith-Ewart method is that for water soluble monomers the validity of the Smith-Ewart theory for particle nucleation has been strongly disputed. Smith-Ewart did a simple assumption in calculating N_p, that the area occupied by an surfactant molecule in a micelle and in a saturated monolayer at the polymer-water interface is the same. This approximation has proven to be satisfactory for hydrocarbon monomers, but has been unsatisfactory in the case of polar monomers [14]. The assumption that micelles capture all the radicals generated in the aqueous phase is reasonable because of the large interfacial area they present, it has subsequently been shown not to be justified. Another assumption made by Smith-Ewart was that the rate of latex particle nucleation remains constant as long as micelles were present. The problem with this is that the number of micelles decreases more rapidly than the number of latex particles increases. A more realistic assumption should therefore be used, i.e. in the case of micelle nucleation the rate of particle formation decrease with time [14].

3.4.5 Monomer partitioning

In bulk and solution polymerizations, reactions occur in a single homogeneous phase, but this is not the situation in emulsion polymerization. In emulsion polymerization multiple phases are present in the reactor and these are normally micelles, monomer droplets, polymer particles (polymer rich phase), and the dispersion medium (i.e. water). Consequently, polymerization progress depends on the kinetic constants and on the concentration of the reactive species in the polymerization loci. In order to describe emulsion polymerization systems by means of mathematical models, it is of paramount importance to implement a reliable prediction of monomer concentration in the different phases. Concentration of monomers in the latex particles are key parameters in determining the polymerization rate. Monomer concentration in the polymer particles can influence the rate of free-radical exit from latex particles, and this will make a alteration in the rate of polymerization. [23]

There are different methods used to calculate monomer distribution in the different phases. Three methods will be explained in Section 5.2.4. The first method is the partition coefficients that was developed first by Gugliotto [19][13]. The second one is a method derived in this work, and this method calculates monomer concentration in polymer particles, and monomer in gas phase and water phase are neglected. The last method is called Flory-Huggins method, and is a thermodynamic approach where monomer in all four phases is calculated. This method is called Flory-Huggins because Flory-Huggins equation is solved. This method requires that pressure is known to calculate amount of monomer in gas and water phase, and pressure is calculated for each interval. Flory-Huggins method is the most comprehensive method of the three mentioned, and this will introduce several parameters in the model.

3.4.6 Molecular weights

A polymer reactor contains polymer with different chain length, and the polymer is characterized by the molecular weight distribution (MWD). This has already been discussed in Section 2.1.2. This can be calculated with moment balances, and some simplifications are made to perform this without solving hundreds of equations. A challenge in modeling of polymerization kinetics is how to reduce a large number of individual species to a tractable solution, and this include both living and dead chains with a significant variation in chain length. A possible solution is to reduce the system of equations through definition of the principle moments of various distributions to track average polymer properties. The equations given will be for a polymerization with one monomer. Moment concentration for the radicals $[\mu_k]$ and dead polymer $[\nu_k]$ distributions is given in Equation 3.4.9 and 3.4.10. [13]

$$[\mu_k] = \sum_{n=1}^{\infty} n^k [P_n] \tag{3.4.9}$$

$$[\nu_k] = \sum_{n=1}^{\infty} n^k [D_n] \tag{3.4.10}$$

These moments definitions will give the infinite set of equations for polymeric species into a subset that are more readily to manage. In different literature it is stated that some of the moments have precise physical meanings. The zeroth live moment, $[\mu_0]$, is the concentration of polymer radicals in the system. The first live moment, $[\mu_1]$, is the concentration of monomer units contained in all growing radicals. [13]

The number-average molecular weight and weight-average molecular weight are defined by using the zeroth, first and second moments of live and dead polymers. These two molecular weights are calculated by using Equation 3.4.11 and 3.4.12. [24]

$$\overline{M}_n = MW_m \frac{\mu_1 + \nu_1}{\mu_0 + \nu_0} \tag{3.4.11}$$

$$\overline{M}_w = MW_m \frac{\mu_2 + \nu_2}{\mu_1 + \nu_1} \tag{3.4.12}$$

As concentration of live polymers is significant smaller than concentration of dead polymers, the contribution of live polymer moments to overall polymer molecular weight is negligibly small. Equation 3.4.11 and 3.4.12 can therefore be reduced to Equation 3.4.13 and 3.4.14. The balances for each moment will be given in Chapter 5.

$$\overline{M}_n \approx MW_m \frac{\nu_1}{\nu_0} \tag{3.4.13}$$

$$\overline{M}_w \approx MW_m \frac{\nu_2}{\nu_1} \tag{3.4.14}$$

Chapter 4

Control of polymerization reactors

The purpose with the modeling in this work is to develop models that are suitable to be utilized for control purpose, and especially for nonlinear model predictive control. Control and measurements of polymerization reactors are a challenge due to complexity of the physical mechanisms and polymerization kinetics. The end-use properties are important for the market value of the different polymers, as polymers are performance materials. Process operation conditions should assure that correct end-use properties reach desired set of target values after the polymerization is finished in the reactor. Linear control theory is not normally utilized in the polymerization field, as the relationship among process operation variables and final molecular and/or end-use properties of polymer materials are strongly nonlinear [13]. A result of this has been a development of more advanced nonlinear control techniques.

In polymerization reactors there are different instabilities and these can be caused by i.e. thermal, viscous, hydrodynamic and kinetic effects [13]. When system viscosity increases there will be a reduction of heat transfer coefficients and this leads to an increase in the reactor temperature. A rapid alteration in reactor temperature gives serious safety issues, and control schemes have to include tight safety procedures. This has to be done in order to guarantee that process operation do not drive into regions of unstable operation. On-line measurements of molecular and end-use properties of polymer materials are difficult, and the control procedures have to rely frequently in values provided by process models and on measured values provided with long delays by plant off-line measurements [13]. A general control solution has to take into consideration the particular characteristics of the analyzed polymerization system, producing consistent, uniform and in-specification polymer. This is a task of the measurements and control system utilized in the polymer process [4]. In order to operate polymer processes safely and in order to set characteristics of the product, a set of process manipulated variables must be kept constant or modified systematically over the duration of the reaction. The cornerstone of successful control strategy is a good mathematical model, and to perform the modeling knowledge about the process is important. The modeling of a general model for semi-batch emulsion polymerization reaction is given in Chapter 5.

4.1 Mathematical dynamic models for control purpose

There are different aspects that have to be considered to decide if a model is suitable for model predictive control. Actually it has to be looked at as a total system, where the model, constraints, control structure, estimator and tuning parameters will determine if it is possible to utilize model predictive control and achieve acceptable results. The mathematical model utilized is important when MPC is implemented, as MPC requires models with satisfying prediction quality. For example if the temperature in the reactor should be controlled, then the model has to be able to predict the temperature's response to the manipulated variables. To control reactor temperature the manipulated variable is usually either inlet coolant temperature, rate of cooling or a combination. This varies for the different emulsion polymerization reactors, and multiple other variables can also be controlled. Models with iterations that take long time to solve makes the model more difficult to implement in MPC, as the calculation time is of critical importance. The model should also be robust, and this means that the model should give acceptable results with different operating conditions and it should be valid over several areas. Different measurements should be available so estimation of the parameters can be performed, which requires several experiments and measurements to achieve reasonable values for the parameters. How suitable a model is for MPC implementation is not readily to discuss before it is implemented.

Modeling of emulsion polymerization will be performed and various sub-models will be derived. These should be suitable for NMPC (see Chapter 5), and various criterias should be attempted to fulfill. These criterias are summarized below.

- The model should be an ODE system, and DAE system should be avoided.
- Stiff system should be avoided, or stiffness reduction should be performed.
- The calculation time should be as rapid as possible, so time-consuming calculations should be avoided if possible.
- Few states are preferred in the model. If there are some rapid dynamic, some states can be solved as steady states.
- The parameters in the model have to be possible to estimate. Estimated parameters will capture mistakes in the model.

4.2 Process control hierarchy

Control structure design for chemical plants, also called plant wide control, consist of the structural decisions of the control system. Control structure design also include how to pair the variables to form the best control loop [3]. These are important issues and decisions around these issues are often based on experience and engineering insight. This is done without considering the details of each problem. A systematic procedure for controlling structure design for chemical plants is important, and a hierarchical approach has proven to be important also in the control of polymer reactors. First the operational and economic objectives are defined and the degrees of freedom available to fulfill the objectives. In a process there are multiple possible measurements and control loops, and the control system can therefore be divided into several layers. These layers are separated by time, and are shown in Figure 4.1.

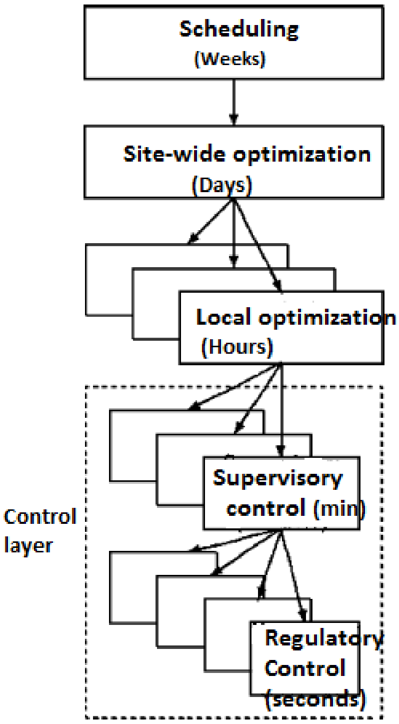

Figure 4.1: Control hierarchy in a plant [3]

New setpoint are recomputed in the local optimization layer and this is done once an hour or so, whereas feedback layers operate continuously. Layers given in Figure 4.1 are linked by controlled variables, and setpoints are computed by upper layer and implemented by lower layer. Selection of these variables is important, and structure design deals with structural decisions that have to be made before designing the controller. These tasks include selections of manipulated variable (inputs), controlled variable (outputs), extra measurements for stabilization, control configuration and controller type. [3]

4.3 Classical control problems in polymerization

4.3.1 Control of reaction rate and reactor temperature

In polymerization, control of reaction rates and reactor temperature are common control problems. Polymerization reactions are exothermic and high activation energy is also presented. This may give different sorts of thermal instabilities. As the activation energy is high, a small increase in reactor temperature will give an increase in reaction rate. This will again lead to a large increase of the rate of heat released. Reaction runaways and increase of reaction rate can occur even if the reactor temperature is constant, this because of nonlinear kinetics

[1]. For a semi-batch process, a secondary feed period may follow, and reactor heat loads alter continuously. Reaction temperature is controlled by manipulating the temperature of water that is circulating through the reactor jacket. To manipulate the jacket temperature in the face of continuously alteration in reactor heat load, a control scheme is required. The reactor temperature is maintained at its desired value, and this is done by adjusting the temperature setpoint for water recirculating through the reactor jacket or the amount or flow rate of the cooling water. [25]

4.3.2 Monomer conversion and polymer production

Control of monomer conversion of the polymer material in the reactor and of the polymer productivity are another possible control problem. The reaction batch time will limit the maximum monomer conversion and polymer production, by existence of diffusional limitations in the reaction medium (glass effect in bulk polymerization) and decay of initiators (free-radical). Increase of monomer conversion and increase of polymer productivity is obtained by manipulation of reaction times, reactor temperature, monomer feed rates and mixtures of initiators. [13]

4.3.3 Control of molecular weight averages and molecular weight distribution (MWD)

In semibatch processes reaction conditions e.g., temperature and monomer concentration, vary along the reaction time. The different reaction rates of all elementary reaction steps that constitute the complex network of the polymerization reaction mechanism will vary along the reaction time. The consequence is that the molecular properties of the produced polymer material alter along the time during transient operation. Drifts of the average molecular weight can be observed along the vessels that constitute the reactor trains of some emulsion polymerization processes. Manipulation of chain transfer agent can be utilized to control the molecular weight averages and of the MWD. Other possibilities to control the main average of the MWD is reactor temperature, initial initiator, monomer feed rates and batch time. Manipulation of reactor temperatures for control of the MWD should be avoided because of safety issues and sluggishness of temperature responses. Manipulation of CTA concentration is preferred at plant site, because manipulation of initiator and monomer composition should also be avoided, as strong coupling with the production targets and with the energy balance variables. [13]

4.3.4 Control of particle size distribution

A fundamental importance is the characteristics of the final particle size distribution of the product. In order to increase the polymer concentration of polymer latex, multi modal particle size distribution may be required. The particle size distribution (PSD) and polymerization rate are coupled in several heterogeneous polymerizations [13]. Measurement of just average

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[1] Nonlinear kinetics are e.g., particle nucleation in emulsion polymerization, reaction inhibition in free-radical polymerization and viscous effects [13]

particle size may not be sufficient. Presence of different size populations resulting in a multi modal distribution could have an effect on final properties and need to be controlled in some situations. There are different particle size measurements available, and these are i.e. optical imaging, election imaging, optical diffraction and scattering and sedimentation [4]. Techniques that gives an indirect measurement of the particle size are measurement of surface tension and conductivity of latexes during emulsion polymerization [13].

4.4 On-line monitoring

To implement advanced closed-loop control strategies, monitoring on polymerization variables is necessary. This is done to ensure a consistent, safe and optimal production of polymeric materials, and to reach desired quality of the product. On-line monitoring give a significant amount of important information about the process, and this can be utilized for modeling, optimization and modifying reaction formulations, even though advanced control is not implemented. Correct information from the on-line monitoring reduces the time-consuming off-line analysis that is performed at the laboratories. [13]

Sensor technology for on-line monitoring of polymerization processes has grown in the last decades, based on more knowledge about advanced control that can also be utilized in other disciplines. Sensors that are utilized for monitoring in polymerization processes can be classified into two different categories. The first one is sensors for monitoring of reactor operation conditions or process variables. These include temperature, flow, pressure and level measurements. These measurements are performed at plant site, and are well established. These variables might be enough to ensure the production of the polymer of interest. The second sensor classification is for monitoring of the trajectory of polymer properties during polymerization. These sensors are more difficult to develop, and they also give useful information to carry on closed-loop control strategies. Even though the development in technology has been enormous, there are still number of important polymer properties that can only be measured in laboratory with time-consuming off-line analysis. These properties are among others MWD, branching and cross linking density, gel content and PSD. Some of the properties that cannot be measured on-line can be found from the measurements of other variables by means of state estimation methods and software sensors that combine mathematical models. [13]

4.4.1 On-line sensors for monitoring polymer quality

Polymerization rate can be measured by several techniques, but calorimetry is often the most convenient technique for industrial reactors. In this technique the heat of reaction is monitored by solving the energy balances of the reactor and the cooling jacket. These measurements are often utilized to evaluate among others monomer conversion. There are other techniques for monitoring the concentration of monomer. Measurements of the MWD of a polymer depend on the nature of the produced polymer, and there are three different classes. The first one is the soluble polymers that are dissolving in a solvent, and the molecular weight can be measured on-line by gel permeation chromatography and light scattering equipment. The other class is insoluble polymers and these do not dissolve in a solvent and have often high molecular weights and often partially or fully cross-linked. The insoluble part is characterized by the insoluble amount, and information about the crosslinking density can be obtained off-line by swelling experiment or spectroscopic techniques. The last class is the polyolefin, and these can be dissolved in chlorinated solvents with high temperatures. Temperature and pressure fractionation equipment are available to measure the MWD of these polymers. For emulsion polymerization there are techniques to perform on-line evaluation of PDS, and one technique is fiber optic dynamic light scattering. [13]

Industrial instruments that require a lot of maintenance and service are desired to be avoided. Other solutions that do not require expensive instruments are of interest. If an on-line measurement of i.e. MWD is impossible, another alternative is to utilize state estimation.

4.5 State estimation

On-line measurements for polymer quality are not always available, and this has been a driving force for the development of state estimators. These estimators have to be capable of estimating polymer properties that are not possible to measure from readily available measurements. The state variable chosen in a process are variables that specify the process at any given time, and these variables are often temperatures and monomer concentration. Real-time information of the state variables are important to perform effective monitoring and control of a process. State estimation provide estimates of the states of the dynamic system, and this is obtained by balancing the contribution made by a deterministic dynamic process model with that given by the measurement model and the actual measurements [13]. This can be given as a mathematical term, and this is given in Equation 4.5.1.

$$\widehat{x}(t) = \int_{0}^{t} f(x,u,\tau)d\tau + K(y(t) - h(x,t)) \tag{4.5.1}$$

In Equation 4.5.1, $\widehat{x}(t)$ is the vector of estimated states $x = [x_1, \ldots x_n]^T$ at time t. The nonlinear process model that is solved from 0 to t is given from $f(x,u,\tau)$. In this model the vector $u(t)$ is a vector with the manipulated input variables and $y(t)$ is the vector of process outputs. Often the process output variable is equal to the state variables; for instance temperature as this can be measured and simultaneously be a state variable. The nonlinear measurement model that is a prediction of measurements based on the estimated state variable is $h(x,t)$ and K is the estimator gain. How the estimator gain is calculated depends on which algorithm that is utilized [13], and estimator gain gives more or less weight to the process model with respect to measurements depending on its value [13]. The contribution of measurements to the estimation of state variables is small if K is small. The value of K may vary along the time and may depend on the measured outputs. In literature of nonlinear control, an Extended Kalman filter (EKF) is an often utilized technique. The challenge with this is a large number of additional tuning parameters from EKF that may complicate online tuning procedures [26].

4.6 Model predictive control

Existence of various operative constraints due to safety or economic, and restrictions related to the valve sizes and actuator dynamics, are all common in chemical process control. All issues given will limit the expected performance of the controlled system, and one well-known control technique is to utilize model predictive control (MPC). Linear model predictive control (LMPC) has found acceptance in today's process industries, due to flexible constraint-handling capabilities as well as its robustness properties. LMPC algorithms utilize a linear process model in prediction and optimization, but this would not work when applied to processes with strong nonlinearities. Polymerization reactor control is highly nonlinear, and control by using nonlinear model predictive control (NMPC) is of interest [26]. For semi-batch reactors utilized for production of high value added polymer but in smaller volumes than in continuous reactor, the controller utilized have to cover a wide range of operating conditions and work good for nonlinear process dynamics. NMPC have a strong potential in improving control and operation of nonlinear processes, and the underlying principle of NPMC is the same as LMPC [26]. The exception is that the model describing the process dynamics is nonlinear when NMPC is utilized. Implementation of NMPC will often pose more technical problems due to computational time and capacity, compared to LMPC. Utilize of NMPC where a nonlinear programming problem is solved on-line requires formidable efforts in order to calculate control actions within fixed sampling time [27].

In MPC a mathematical dynamic model of the process is utilized to predict the current values of the output (controlled) variables. The model is often implemented in the form of a multi variable linear or nonlinear difference equation. The equation can be found from data collected during plant tests that consist of input variables or a disturbance variable changing from one value to another when series of step alters with different durations are utilized [4]. The structure of MPC is shown in Figure 4.2. The difference between the predicted and actual output variables, serve as a feedback signal to the prediction block and are utilized in two types of control calculations that are performed at each sampling instant. These are set point and control calculations.

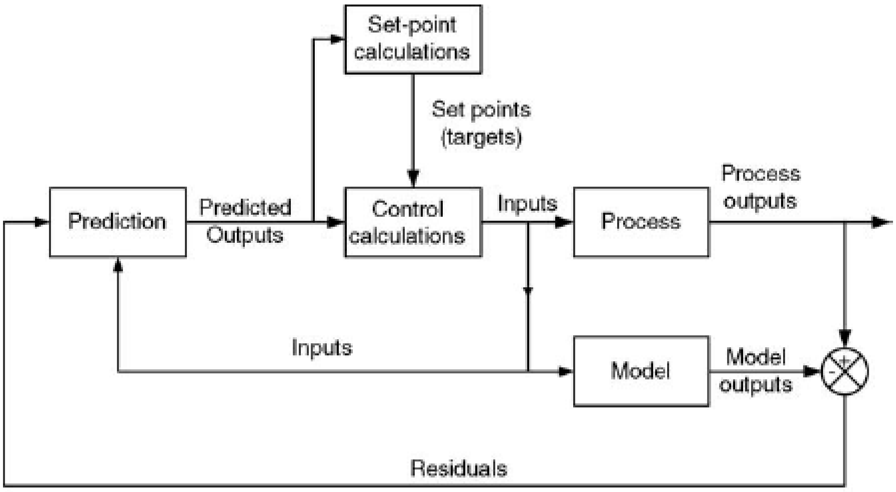

Figure 4.2: Structure of model predictive control [4]

An advantage of MPC is that inequality constraints can be incorporated in both the setpoint and control calculations. These constraints are a result of physical limitations on plant equipment, and setpoints for control calculations are often calculated from an economic optimization of the process based on a steady state process. Objective of the control calculations in the control block is to determine a sequence of control moves, so predicted response moves to the setpoint in an optimal manner. This can be done by following a reference trajectory [4]. Calculated control actions are implemented as setpoint to the regulatory control layer. The quality of MPC dependents on an accurate process model that has to be available and this model have to capture interactions between input, output and disturbance variables.

4.7 Safety and control issues in polymerization reactors

In chemical industry accidents can happen. Primary causes are technical failures, human failures and problems with the chemical reactions. Polymerization reactions are subjects to thermal runaway, and this can cause accidents. To avoid accidents different attempts can be utilized and this is maintenance of equipment and facilities, qualification and training of operators, better knowledge of the thermo-chemistry and reaction kinetics. Automation and on-line control are important to prevent technical and human failure. It is normal that when advanced control strategies are implemented, safety is considered as a hard constraint during the process optimization step. [13]

There are in polymerization reactors multiple steady states, and this is known both experimentally and theoretically. As polymerization reactors are exothermic and reactor thermal runaways can occur, effective control strategies have to be implemented. When there are several steady states present, numerous stable steady states are possible; one example is the situation with extremely low or high monomer conversion. For economic and practical reasons this cannot be chosen as the reactor operating point, and it may be necessary to choose an unstable steady state at intermediate conversion as the reactor operating point. Another challenge is that on-line measurements of i.e. polymer molecular weight, composition and degree of branching are not always available. Control engineers have to rely on polymer properties from laboratory analysis of reactor samples or from analysis of the final product. This will make control more difficult, as these measurements had been advantageous to have. The control system for a polymerization reactor should be robust to handle unmeasured disturbances which can impact the operation of the polymer reactor. The variability within batch reactor and variability from batch to batch as the reactor produce different grades is also a challenge when the control setup is decided. The control strategy has to be readily adapted to a multi-product plant and in some cases to on-line grade transition. Another problem that can affect the control system is the time of formation of a single chain that is only a small fraction of the batch time. This results in inhomogeneity as polymer chains can be formed under different conditions during the course of the batch time. This can make problem for composition control, because polymer chains formed early in the reaction may contain a higher fraction of the more reactive monomer (this is in co-polymerization) than the chains formed later in the reaction. A solution to this problem is to operate the reactor under the so-called starved feed policy. Monomer is fed into the reactor to maintain a constant rate of reaction, and the reaction environment is kept constant during the batch. [4]

Chapter 5

Modeling: Emulsion polymerization processes

Emulsion polymerization is a complex heterogeneous process involving transport of monomers, free radicals and other species between both aqueous and organic phases. Emulsion polymerization is known to be the most complicated system, compared to suspension or precipitation polymerization [16]. A challenging problem is therefore to develop fundamental mathematical models for the polymerization reactor. Models are valuable as they offer a powerful tool for process control, monitoring, optimization, scale-up and operator training. Models also give a better understanding of underlying mechanisms in the process. Examples are reaction mechanism, physical transport phenomena (e.g. mass and heat transfer and mixing), reactor type and reactor operating conditions that will affect the ”polymer quality” of the final product [12].

Different factors make modeling of the system difficult, i.e. polymerization rate in the organic phase is not only controlled by monomer partitioning, but it is also influenced by particle nucleation and radical absorption and desorption. Particle stability is affected by surfactant type, amount of surfactant and ionic strength of the dispersion media. Other difficulties in modeling of emulsion polymerization are the numerical intensity in solving sets of nonlinear ordinary differential equations combined with algebraic equations. Lack of information on certain model parameters will make adjustments towards a real process complex.

In literature there are several models describing different aspects of emulsion polymerization. The problem is that most of these models deal with specific aspects in emulsion polymerization and are not general models that can readily be utilized for other process conditions and control purpose. The objective is therefore to develop a more general model; this model should be simple and cover both physical and chemical phenomena in emulsion polymerization. Models like this consist of a set of differential equations combined with algebraic equations, based on mass, energy and population balances.

5.1 Elements of polymerization models

A model of an emulsion polymerization process consist of multiple sub-models or elements, these are eventually combined to yield the final global polymerization model. These sub-models are listed below. It is worth noting that not every sub-model has to be included to build a final global model. There can be other elements included in the global model that is not listed below. [28]

- Reaction kinetics
- Thermodynamics
- Mass transport
- Particle kinetics

The reaction kinetics sub-model consists of mass and population balance equations. These equations are derived based on elementary reaction given in the reaction mechanism. Usually, this is a system of differential and/or algebraic equations that can be solved using various numerical methods. In the thermodynamics of a polymerization system there are several approaches with different levels of complicity, and this describes phase behavior and phase partitioning of a polymerization system. Simple partition coefficients can be utilized, but complex equation of state and activity coefficient models can also be utilized. Sub-models for thermodynamics consist usually of a set of non-linear algebraic equations, and these are solved simultaneously with the differential mass balances. [28]

A model describing the particle kinetics should be developed, and this can contain description of particle formation (nucleation), particle coagulation and in some cases also particle breakage. To describe the particle kinetics in a polymerization system there are various approaches found, e.g. assuming instantaneous nucleation that yield equal-sized spherical particles of constant number (no coagulation). More detailed sub-models can include particle formation by both homogeneous and heterogeneous nucleation, and this can be followed by particle coagulation. Particles can then be described as equal-sized spheres or as a distribution of a range of sizes. DLVO-theory, that describes force between charged surfaces interacting through a liquid medium, can be utilized to account for the role of surfactants or stabilizer. [28]

Mass transport effects are important in polymerization systems, as diffusion limitations affect both chemical rate constant and interphase mass transport. Interphase mass transport can be described by film theory and correlations for mass transfer coefficients are utilized. A diffusion limitation on polymerization reactions that often occur are cage; glass and gel effect. The decrease of initiator efficiency is explained by the cage effect. Glass and gel effects denote the reduction of propagation and termination reaction coefficients. To accurately describe mass transport effects, models to evaluate diffusion coefficients of monomers and polymers chains are needed. Often these diffusion coefficients are not known, and other simpler methods should be utilized in modeling of mass transport. [28]

5.2 Dynamic mathematical modeling

In this section different variables in an emulsion polymerization process have been modeled. These variables will together constitute a complete dynamic mathematical model of an emulsion polymerization semi-batch reactor. It was possible to model the same variable in different ways, and in this work this was performed for some variables. This was done to make the model simpler and to have more options depending on parameters available from measurements or literature. Mass and energy balances were derived for a semi-batch process, and these are readily to expand to an account for both batch and continuous processes. The energy balance were derived to make post-dosing of chemicals possible, as these chemicals may have a cooling effect if the temperature of the chemicals are lower than the reactor mixture. The model can predicts i.e. monomer concentration in the gas, aqueous, monomer-rich and polymer-rich phases, the overall monomer conversion, the polymerization rate, average number of radicals per polymer particle, reactor temperature, outlet cooling temperature, pressure etc.

5.2.1 Typical assumptions utilized in modeling

Different assumptions are utilized when a dynamic mathematical model is derived for an emulsion polymerization semi-batch reactor. Some assumptions are normal to utilize, and some are required to make the model fit its purpose. These are listed below. Other assumptions will be given when they are utilized in the modeling.

- Model nucleation occurs through classical micellar mechanism because of high surfactant concentration. The other type of nucleation, homogeneous nucleation, is considered negligible.
- Monomer droplet diameter as well as those of the growing particles is considered to be monodisperse.
- Propagation and termination in the aqueous phase are neglected.
- Transfer to polymer reaction is not considered much in this work.
- Coagulation between particles is neglected. The extension of coagulation is often not known, and it is not readily to include in the model.
- The mixture in the reactor is assumed to be perfectly mixed.

5.2.2 Kinetics

The reaction kinetic has already been given in Section 3.2, and these reactions have been utilized in the modeling part.

Reaction rates

Only the most important reactions were considered to make the model more manageable. If more kinetic is considered several rate constants have to be known, and often no information is available about these. To estimate all parameters that are included in the model, different measured values have to be known and available. As the purpose is to utilize the model for NMPC the model has to be made simple and therefore only give the most important kinetics.

Arrhenius law

The reaction rate depends on the reactor temperature, so if temperature increase the reaction rate increase. Quantitatively this relationship between the rate a reaction proceeds and its temperature, is determined by the Arrhenius equation given in Equation 5.2.1. Arrhenius equation is a simple formula for the temperature dependence of the reaction rate constant, and therefore, rate of a chemical reaction. If reactor temperature is not constant, the rate constants are not constant through the batch. To study how the rate constants change with temperature Arrhenius equation is utilized, but activation energy (E_j) and frequency factor (A_j) have to be found experimental or in this case in literature.

$$k_j = A_j e^{(\frac{-E_j}{RT_R})} \tag{5.2.1}$$

In literature, E_j and A_j are found by experiment for a given temperature. This temperature is often higher than the typical temperature in a emulsion polymerization reactor. Another version of Arrhenius equation was utilized to correct for this. This equation is self-explaining, and given in Equation 5.2.2. Values for E_j and A_j for a specified temperature was utilized to calculate a rate constant for a given temperature, and this temperature is utilized as a reference temperature.

$$k_j = k_{j,ref} e^{(\frac{-E_j}{R}(\frac{1}{T_R} - \frac{1}{T_{ref}}))} \tag{5.2.2}$$

Initiator decomposition

Initiator is consumed by thermal decomposition in the aqueous phase, and the corresponding reaction rate is given in Equation 5.2.3. Moles of every specie were decided to utilize in the modeling, but in literature it is normal to give the species in concentration.

$$R_I = k_I[I]_w V_W = k_I N_{ini} \tag{5.2.3}$$

Chain initiation is given by the rate coefficient of the initiator (see Equation 5.2.4), and it is important to include an efficiency factor for the initiator.

$$R_{init} = 2fk_I N_{ini} \tag{5.2.4}$$

A thermal free radical initiator should be relative stable at room temperature, but in polymer-processing the temperature will decompose the initiator. The decomposition rate (k_I) of the initiator will also depend on the solvent/monomer system. The effect of solvent molecules, also called the cage effect, causes secondary wastage reactions including recombination of radicals to regenerate the initiator [29]. As viscosity in the solution increase, this cage effect becomes more significant. An indicator of activity of an initiator is its half-life, $t_{1/2}$, and if this is known for two or more temperatures the frequency factor and activation energy can be found. The half-life of an initiator is the time required to reduce the original initiator content of a solution by 50%, at a given temperature. The initiator decomposition rate is found from Equation 5.2.5, where it is assumed first order decomposition kinetics. This is a normal assumption to make for some initiators. In literature the half-life of the initiator is often readily to find information about. From two half-lives for a given temperature, the activation energy can be found, as given in Equation 5.2.6.

$$k_I = \frac{\ln 2}{t_{1/2}} \tag{5.2.5}$$

$$E_I = \frac{RT_1T_2}{(T_1 - T_2)} \ln(\frac{k_1}{k_2}) \tag{5.2.6}$$

Polymerization rate

In this work, the rate of polymerization expression follows from the method utilized to calculate the radical distribution in the polymer particles. The expression given in most literature is where the average number of radicals per particle has to be known. This way of calculating the rate of polymerization is given in Equation 5.2.7. Polymerization rate has the units moles/s,l in most literature. This is because N_p is given as number of particles per unit volume of water. Since R_p is only utilized in the mole balance for monomer and in this balance R_p is multiplied with the water volume it can be decided to calculate N_p in moles. Then it is not necessary to multiply with volume in the mole balance of monomer. The method utilized for calculation of N_p has to have the units number of particles or moles of particle, where N_A is utilized to give the correct unit. Moles of particles will be used further, and it is not necessary to divide Equation 5.2.7 with N_A. Another way to express polymerization rate is to calculate total amount of radicals in the reactor and radicals in water phase. This can be utilized to calculate amount of radicals in the particles and utilize this directly to find the rate of polymerization through the batch. This is given in Equation 5.2.8. A more comprehensive explanation will be given later about how the expression in Equation 5.2.8 was found.

$$R_p = k_p[M]_p N_p \bar{n} \tag{5.2.7}$$

$$R_p = k_p[M]_p (N_R - N_{rw}) \tag{5.2.8}$$

Termination

Termination can occur from two different reactions and these are by combination or disproportionation. The termination affects polymer molecular weight; thus termination is often expressed by a total termination rate coefficient k_t ($k_t = k_{tc} + k_{td}$). This rate constant is possible to find information about for each monomer, i.e. in the Polymer Handbook. Information needed in the model is the rate coefficient k_t, and this is often given in the unit $\frac{l}{mole,s}$. Arrhenius equation can be utilized to calculate termination when temperature is changed. The rate of radical termination in the polymer particles with j radicals is given in Equation 5.2.9. This is utilized in different parts of the modeling, i.e. in the balance of particles with j radicals.

$$R_t = \frac{k_t}{v_p N_A} j(j-1) \tag{5.2.9}$$

Other reaction rates

Both the rate constant for desorption (k_{de}) and absorption (k_a) of radicals is utilized in the modeling, and these are especially important in the radical distribution part. The physical mechanism by which such entry of radicals takes place has been debated among scientists. Smith and Ewart proposed that radicals will enter because of absorption, but i.e. Barrett proposed that radical entry happens by irreversible absorption due to collision [18]. Collision or diffusion theories will not be utilized, as these will introduce more parameters that are unknown. Desorption rate constant is not readily to calculate or find, and calculation of this will introduce several new parameters into the model. All these parameters have to be estimated, or for some processes they are available in literature. The rate desorption constant will change with temperature, particle size (i.e. diameter) etc., but there are different methods in literature that give equations to calculate k_{de} [20] [30]. The units for both desorption and absorption rate coefficients are in s^{-1}. If these rate coefficients are not found in literature they should be estimated, but they are not constant through the process.

Transfer to monomer, polymer, solvent, etc., can also be counted for if information about this is available. The moment balances will be derived and a MATLAB model that includes the moment balances will be given in the library. If information is not given about these transfer reactions, the transfer rate constants can be set to zero, and the moment balances is not utilized. The same is for the rate constant for an inhibitor, as this will also be included in the model, but information is needed to be able to utilize this in the modeling.

5.2.3 Energy and material balances

A fundamental law of physics state that mass cannot be produced nor destroyed, and mass is therefore conserved. Equally fundamental is the law of conservation of energy. Energy can change its form, but it cannot be created or destroyed. These two laws of physics provide the basis for two tools which are utilized in engineering and science; energy and material balances. Energy and material balances are important in industry, and material balances are fundamental to the control of processing, and especially in control of yields of the product. As the energy cost has increased the last years, industries have to find methods to reduce energy consumptions in processing. Energy balances are important for this reason, and they are utilized in the examination of the various stages of a process, and over the whole processes.

Unsteady-state energy balances

Energy takes different forms, i.e. heat, kinetic energy, chemical energy and potential energy. Because of interconversion it is not always readily to isolate separate constituents of energy balances, but under some circumstances certain aspects predominate. If the various forms of energy entering into a process is unfamiliar it is clever to put them all down, and after preliminary calculations the important ones emerge and other minor ones can be lumped together or in some cases ignored. The first energy balance is for the reactor, and this is utilized to calculate reactor temperature through the batch (See equation 5.2.10). A more elaborative explanation about the derivation of the energy balance is given in Appendix A.5. The energy balance is for a semi-batch reactor, and the last term on the right hand side is for post-dosing of chemicals. Post-dosing can have a cooling/heating effect on reactor mixture. The first term is the heat of reaction, the second term the heat loss to the environment from the top of the reactor and the third term is the heat transfer from the reactor to the cooling jacket.

$$\frac{dT_R}{dt} = \frac{R_p \Delta H_{p,rxn} - U_t A_t (T_R - T_a) - UA(T_R - T_{ave}) - W_{in} c_{in} (T_R - T_{in})}{m c_{pmix}} \tag{5.2.10}$$

The second energy balance can be utilized to calculate outlet temperature of the cooling jacket. The cooling jacket could have been modeled as multiple sections, but instead only inlet and outlet temperature are considered. An average temperature is utilized, as control of the reactor temperature becomes simpler to perform. The energy balance for the cooling jacket is given in Equation 5.2.11. The first term is rate of energy added and removed to the system by the water mass flow in the jacket. The second term is heat loss to the environment and the last term is for the heat transfer from the jacket to the reactor. As no energy balance for the temperature of the reactor metal is utilized, a term in the denominator is included as the steel of the reactor has to be cooled or heated. There is actually a temperature gradient in the reactor steel. It is possible to make a balance for the metal temperature, and utilize this as a state. This will make some change in the two other balances, but this was not utilized as at least one more heat transfer coefficient had to be estimated.

$$\frac{dT_{j,out}}{dt} = \frac{W_c c_{pw} (T_{j,in} - T_{j,out}) + U_a A_a (T_a - T_{j,out}) + UA(T_R - T_{ave})}{(m_w c_{pw} + m_m c_{pmet})} \tag{5.2.11}$$

Material balances

Chemical engineers do a mass balance to account for what happens to each of the chemicals that is utilized in a chemical process. As the process considered in this thesis is involving chemical reactions, it must be accounted for the formation of product chemicals and the consumption of feed chemicals. A mole/mass balance has to be written for each chemical, and account its formation and consumption. When reaction rate are known, mass or mole balances can be outlined in a general form. These balances will be presented for the most extended case of this work, semi-batch. Monomer, initiator, and surfactant amount in reactor was utilized as states and mole reacted monomer can readily be calculated. The mole balance for monomer is given in Equation 5.2.12.

$$\frac{dN_m}{dt} = F_{m,in} - R_p \tag{5.2.12}$$

Initiator is consumed by thermal decomposition in the aqueous phase, and the balance for initiator is given in Equation 5.2.13. Equation for surfactant is given in Equation 5.2.14.

Surfactant will not react or be consumed, but increase stability in the reactor mixture.

$$\frac{dN_{ini}}{dt} = F_{I,in} - k_I N_{ini} \tag{5.2.13}$$

$$\frac{dF_s}{dt} = F_{s,in} + F_{s,post-dosed} \tag{5.2.14}$$

Reacted monomer is readily calculated from Equation 5.2.15, and $F_{m,in} = \widetilde{N_m}$. This is actually a state, which can be replaced by a state that gives reacted monomer. $\widetilde{N_m}$ is often chosen as a state, as states for all chemicals that are dosed in the reactor is wanted. This can be utilized to calculate monomer conversion and this is given in Equation 5.2.16.

$$N_{reacted,monomer} = \widetilde{N_m} - N_m \tag{5.2.15}$$

$$X = \frac{\widetilde{N_m} - N_m}{\widetilde{N_m}} = 1 - \frac{N_m}{\widetilde{N_m}} \tag{5.2.16}$$

If chain transfer agent and inhibitor is utilized, two more mole balances are given (See Equation 5.2.17 and 5.2.18)

$$\frac{dN_{CTA}}{dt} = F_{CTA,in} - \frac{k_{fcta}[CTA]_p N_p \bar{n}}{N_A} = F_{CTA,in} - k_{fcta}[CTA](N_R - N_{rw}) \tag{5.2.17}$$

$$\frac{dN_Z}{dt} = F_{Z,in} - k_z[Z]_p \frac{N_p \bar{n}}{N_A} = F_{Z,in} - k_z[Z]_p(N_R - N_{rw}) \tag{5.2.18}$$

5.2.4 Monomer partitioning

Three different methods for calculation of monomer distribution have been found, as monomer concentration in the polymer particles has to be known to calculate the polymerization rate. Equation for these three methods will be given, and an explanation of how to find monomer concentration in the different phases for the three intervals in emulsion polymerization. The first method is the partition coefficients method, the second method is a simple method derived in this work and the last method is a thermodynamic approach that utilizes Flory-Huggins equation to calculate the amount of monomer in all four phases.

Partition coefficients

This method is given because in multi-monomer system calculation of concentration of monomer in different phases involves simultaneous solution of the thermodynamic equilibrium equations and material balances. Equilibrium equations based on both Flory-Huggins equation and partition coefficients are utilized. The problem is that for multi-monomer system, the parameters of the Flory-Huggins equation are not readily to find, or not available. The partition coefficient method can therefore be utilized, where partition coefficients have to be available for the system. The partition coefficients of monomer j between the monomer droplets and the aqueous phase, K_{d-aq}, and between the water and the particles, K_{aq-p}, are given in Equation 5.2.19 and 5.2.20.

$$K_{d-aq} = \frac{V_{md}/V_d}{V_{m,aq}/V_{aq}} \tag{5.2.19}$$

$$K_{aq-p} = \frac{V_{m,aq}/V_{aq}}{V_{m,p}/V_p} \tag{5.2.20}$$

V_d, V_{aq} and V_p are the overall volume of droplets, aqueous phase and monomer swollen particles. If σ that is a coefficient related to the saturation degree of the particles is available, the partition coefficients between the monomer droplet and the aqueous phase, K_{d-aq}, can be calculated. This is given in Equation 5.2.21. [19]

$$K_{d-aq} = \frac{\sigma}{K_{aq-p}} \tag{5.2.21}$$

For each of the mentioned phases in the process there are given an equation, except for the gas phase. Equation for a system with one monomer is given, but it is readily to expand it to account for multi-monomer processes. In Equation 5.2.22, φ is the volume fraction of water. [19]

$$V_{aq} = \varphi V_r + V_{m,aq} \tag{5.2.22}$$

$$V_p = V_{pol} + V_{m,p} \tag{5.2.23}$$

$$V_d = V_{m,d} \tag{5.2.24}$$

The partition of monomer is given in Equation 5.2.25. The concentration of monomer in the polymer particles is given in Equation 5.2.26. At last the total polymer particle volume V_p is given in Equation 5.2.27. All equations give monomer partition by the simultaneous resolution of these equations.

$$[M]V_r\frac{MW_m}{\rho_m} = V_{m,d} + V_{m,aq} + V_{m,p} \tag{5.2.25}$$

$$[M]_p = \frac{V_{mp}\rho_m}{V_p MW_m} \tag{5.2.26}$$

$$V_p = ([M]_0 - [M])\frac{MW_m V_r}{\rho_p} \tag{5.2.27}$$

For some emulsion polymerization process, partition coefficients of the monomer between the monomer droplets and the aqueous phase, K_{d-aq}, and between the water and the particles, K_{aq-p}, is possible to find in literature. This method could therefore be utilized, and it is readily to implement and solve in MATLAB. Amount of monomer in the gas phase is not calculated from this method, but this is possible to include but the fugacity should probably be known. It is possible to set all the equations in a given order so that they can be solved as intermediate calculations. A DAE system is therefore not needed if this method is utilized in combination with the mole-balances.

Simple method; Concentration of monomer in the polymer particles

Complete descriptions of the thermodynamics of partitioning of monomers between the different phases (aqueous, monomer, polymer particles and gas) is complex and requires knowledge of many quantities that are difficult to measure. These quantities can be interaction parameters and interfacial tensions. This is the reason for using a simple method that neglect monomer in gas and water phase. It is assumed that amount of monomer is low compared to amount of monomer in the polymer particles. A second method to calculate M_p and V_p in Interval II and III was therefore derived. The derivations of these equations are found in Appendix A.3. For Interval II, concentration of monomer in the polymer particles and the overall volume of the polymer particles are given in Equation 5.2.28 and 5.2.29. In these equations x_c is the critical conversion, and this can be found from measured process data or it can be calculated.

$$[M]_p = \frac{(1-x_c)\rho_m}{(1-x_c+x_c\rho_m/\rho_p)MW_M} \tag{5.2.28}$$

$$V_p = MW_m X \widetilde{N}_m [\frac{1}{\rho_p} + \frac{1}{\rho_m}(\frac{1}{x_c} - 1)] \tag{5.2.29}$$

For Interval III, concentration of monomer in the polymer particles and overall volume of the polymer particle is given in Equation 5.2.30 and 5.2.31.

$$[M]_p = \frac{(1-X)\rho_m}{(1-X+X\rho_m/\rho_p)MW_M} \tag{5.2.30}$$

$$V_p = MW_m \widetilde{N}_m [\frac{X}{\rho_p} + \frac{1-X}{\rho_m}] \tag{5.2.31}$$

From this simple method the pressure can be found, and the derivation of this is given in Appendix A.3. Pressure for Interval II and III is given in Equation 5.2.32 and 5.2.33.

$$P = P_{sat} \tag{5.2.32}$$

$$P = \alpha_m P_{sat} \tag{5.2.33}$$

In these equations $P_{sat} = P_{m,sat} + P_{w,sat}$. The activity is found from Equation 5.2.34 for Interval III, as $\alpha_m = 1$ in Interval II.

$$\alpha_m = \frac{1-X}{1-x_c}\frac{x_c}{X} \tag{5.2.34}$$

Thermodynamic approach; Amount of monomer in all phases

The other methods that calculate the monomer concentration in the polymer particles has not considered the amount of monomer in all phases. Amount of monomer in both gas and water phase is probably a small amount compared to the monomer rich phase (monomer droplets) that exist in Interval II and the polymer rich phase. To be able to check if this assumption influences the model predictions and if the simple method gives satisfying results, a method that can calculate amount of monomer in all phases has to be found. The method derived will predict amount of monomer in all phase but it requires reactor pressure, and pressure in both Interval II and III has to be calculated.

The vapor phase in the reactor occupies the free space on the top of the liquid mixture, and the gas phase consist mainly of water and monomer. Reactor pressure can therefore be modeled as the sum of monomer and water vapor pressure, but this can only be utilized when there exist a separate monomer phase in the liquid mixture. This is for Interval II, and do not account when critical conversion is reached. The aqueous phase consists of water and monomer dissolved in it. In Interval III there is no longer a separate monomer phase and the pressure drops in the reactor. [7]

During Interval II the monomer/polymer ratio remains constant because of the equilibrium solubility of monomer in the polymer phase. In the following calculation the four phases are assumed to be in equilibrium during polymerization, and this results in an equal fugacity of VCM in the different phases (See Equation 5.2.35). [7]

$$f_m^g = f_m^w = f_m^m = f_m^p \tag{5.2.35}$$

From the equilibrium assumption, pressure in the reactor can be calculated through the following thermodynamic considerations. Fugasity coefficient of monomer in the binary vapor mixture is given in Equation 5.2.36, and in this equation the second virial coefficients will give monomer solubility constant, δ_{mw}, as given in Equation 5.2.37. How to calculate the virial coefficient can be found in Appendix A.8. [7]

$$\ln(\varphi_m) = \ln(\frac{f_m^g}{P_m}) = \ln(\frac{f_m^g}{y_m P}) = \frac{P}{RT_R}[B_m + (1 - y_m)^2 \delta_{mw}] \tag{5.2.36}$$

$$\delta_{mw} = 2B_{mw} - B_m - B_w \tag{5.2.37}$$

Mole fraction of monomer in the vapor phase can be calculated if fraction of water vapor is given. An assumption is made that water vapor partial pressure is equal to its saturation value, and this is given in Equation 5.2.38. [7]

$$y_m = 1 - y_w = 1 - \frac{P_w^{sat}}{P} \tag{5.2.38}$$

Next an equation that can be utilized to calculate the monomer activity is found, and Flory-Huggins equation is utilized for this purpose, see Equation 5.2.39. As Flory-Huggins equation is used, this method for calculation of monomer amount is called Flory-Huggins method.

Monomer activity has to be calculated in Interval III. In Interval II, Flory-Huggins equation is utilized to calculate the polymer volume fraction in the polymer rich phase (φ_p) as the monomer activity is equal to one [7]. Flory-Huggins interaction parameter (χ) has to be calculated, and this is given in Appendix A.7. This parameter is an empirical parameter named after Flory, and the value of the interaction parameter depends on nature and composition of the system [31].

$$\ln(\alpha_m) = \ln(1-\varphi_p) + \varphi_p + \chi\varphi_p^2 \tag{5.2.39}$$

It has already been mentioned that in Interval II, the reactor pressure is equal to the sum of monomer and water vapor partial pressure, and it is assumed that vapor partial pressure is equal to its saturation value. For Interval III a combination of equation 5.2.35, 5.2.36 and 5.2.39 is utilized to obtain Equation 5.2.40 that can be utilized to calculate the pressure in Interval III. This equation have to be solved with iteration, and a function named *fsolve* in MATLAB can be utilized. To avoid this iteration the pressure can be found from $P = a_m P_{sat}$. [7]

$$f_m^p = f_m^g \Rightarrow \alpha_m f_m^0 = \varphi_m y_m P f_m^0 \exp(\ln(1-\varphi_p) + \varphi_p + \chi{\varphi_p}^2) = y_m P \exp(\frac{P}{RT_R}(B_m + (1-y_m)^2\delta_{mw}) \tag{5.2.40}$$

Before the equations utilized to calculate amount of monomer in the different phase is given, the fugacity is found from Equation 5.2.41 where the gas phase virial equation of state is utilized. This can be directly utilized in Interval II, where pressure is calculated from $P = P_w^{sat} + P_m^{sat}$, and equation 5.2.40 is not necessary to utilize in this interval. After this the compressibility factor of the gas is calculated in Equation 5.2.42. [32]

$$\ln(\frac{f_m^g}{y_m P}) = \frac{B_1 P}{(RT_R)\cdot 1000} \Rightarrow f_m^g = y_m P e^{(\frac{B_1 P}{(RT_R)\cdot 1000})} \tag{5.2.41}$$

where $B_1 = B_m + y_w^2(2B_{wm} - B_m - B_w)$.

$$z = 1 + \frac{B_2 P}{RT_R} \tag{5.2.42}$$

where $B_2 = y_m^2 B_m^2 + y_w^2 B_w^2 + 2y_m y_w B_{wm}$.

As Interval I is short, the amount of monomer in the different phases is calculated for Interval II and III, so the calculations in Interval II, will account from X=0 to the critical conversion is reached (change to Interval III). In Interval III there is not a separate monomer phase in the reactor mixture. For both Interval II and III, the amount of monomer and water in the gas phase are calculated from Equation 5.2.44 and 5.2.45. To be able to calculate this, the volume of the gas phase has to be found. This volume can be found in different ways, where two different equations were tested, and as they gave the same answer one of them is given, see Equation 5.2.43. In this equation fugacity of water in gaseous phase has to be known, and this is found from $f_w^P = P - f_m^g$. [7] [32]

$$V_g = [\frac{V_R - (\frac{M_0}{\rho_m}(1-X)) - \frac{W_w}{\rho_w} - \frac{M_0 X}{\rho_p}}{(1 - \frac{1}{RT_R}(\frac{f_m^g MW_m}{\rho_m} + \frac{f_w^g MW_m}{\rho_w}))}] \tag{5.2.43}$$

$$W_g = \frac{y_w V_g P}{zRT_R} MW_w \tag{5.2.44}$$

$$M_g = \frac{y_m V_g P}{zRT_R} MW_m \tag{5.2.45}$$

Amount of monomer in the water phase, is calculated by equation 5.2.46. In this equation K_1 is the monomer in water solubility constant. [7] [32]

$$M_w = K_1 \frac{P_m^{sat}}{P}(W_w - W_g) \tag{5.2.46}$$

Interval II

Remember that pressure is found from $P = P_m^{sat} + P_w^{sat}$ and this can be utilized to calculate mole fraction of water vapor, fugasity, etc. Amount of monomer in the monomer rich phase is given by equation 5.2.47 and amount of monomer in the polymer rich phase is given by equation 5.2.48. [7]

$$M_m = M_0(1 - \frac{X}{x_s}) - M_w - M_g \tag{5.2.47}$$

$$\begin{aligned} M_p &= M_0 \tfrac{X}{x_s}(1 - x_s) \\ x_s &= \tfrac{\varphi_p \rho_p}{\varphi_p \rho_p + (1-\varphi_p)\rho_m} \end{aligned} \tag{5.2.48}$$

The volume of monomer in monomer rich phase and polymer rich phase is given in Equation 5.2.49, and at last the concentration of monomer in both phases are given in Equation 5.2.50. [7]

$$\begin{aligned} V_m &= \tfrac{M_m}{\rho_m} \\ V_p &= \tfrac{M_p}{\rho_m} + \tfrac{M_0 X}{\rho_p} \end{aligned} \tag{5.2.49}$$

$$\begin{aligned} [M]_m &= \tfrac{\rho_m}{MW_m} \\ [M]_p &= \tfrac{M_p}{MW_m V_p} \end{aligned} \tag{5.2.50}$$

Interval III

In this interval pressure is calculated by using Equation 5.2.40, but first the polymer volume fraction in the polymer rich phase is found from the mole balances. This fraction is utilized further to calculate monomer activity by Flory-Huggins equation (See Equation 5.2.39). The pressure can be solved with iteration (See Equation 5.2.40). Equations for calculation of amount of monomer in gas and water phase have already been given, as these are the same that were utilized in Interval II. In Interval III, there is no longer a separated monomer phase and amount of monomer in polymer rich phase is calculated from Equation 5.2.51. [7]

$$M_p = M_0(1 - X) - M_w - M_g \tag{5.2.51}$$

5.2.5 Number of radicals per polymer particle

The dynamic balance for moles of particles *N(j)*, containing *j* radicals, was given in Section 3.4.3. The balance can be solved dynamic and introduce several differential equations in the model, as *N(j)* is a state. The number of states depends on how large the *j* value is decided to be. Initial values are then required and the initial values may be important to know something about as this is a nonlinear model. If the balance for *N(j)* are solved dynamic for a specified number of *j*, moles of particles do not need to be a state in the model. This is because $N_p = \sum_{j=0}^{\infty} N(j)$. A set of dynamic equations have to be solved and these are given in Equation 5.2.52. The rate of entry is given as $k_a N_{rw}$, and k_a is the entry rate coefficient and this has to be estimated for each system. N_{rw} includes radicals of any length, and this is given in mole. The two first equations give moles of particles with zero and one radical (j=0 and j=1). For j > 1 the third equation in 5.2.52 is utilized. For numerical implementation, the maximum number of radicals per particle (j_{max}) is fixed. It is assumed that when a radical enters into a particle containing j_{max} radicals, a termination will happen instantaneous. The two last differential equations are for j_{max} and j_{max-1}.

$$
\begin{aligned}
\frac{dN(0)}{dt} &= -k_a N_{rw} N_A N(0) + \frac{2k_t}{v_p N_A} N(2) + (k_{zp} Z_p + k_{de}) N(1) \\
\frac{dN(1)}{dt} &= k_a N_{rw} N_A (N(0) - N(1)) + \frac{6k_t}{v_p N_A} N(3) - (k_{zp} Z_p + k_{de})(N(1) - 2N(2)) \\
\frac{dN(j)}{dt} &= k_a N_{rw} N_A (N(j-1) - N(j)) + \frac{k_t}{v_p N_A}((j+2)(j+1)N(j+2) - j(j-1)N(j)) \\
&\quad -(k_{zp} Z_p + k_{de})(jN(j) - (j+1)N(j+1)) \\
\frac{dN(j_{\max}-1)}{dt} &= k_a N_{rw} N_A (N(j_{\max}-2) - N(j_{\max}-1) - N(j_{\max})) - \frac{k_t}{v_p N_A}((j_{\max}-1)(j_{\max}-2) \\
&\quad N(j_{\max}-1)) - (k_{zp} Z_p + k_{de})((j_{\max}-1)N(j_{\max}-1) - (j_{\max})N(j_{\max})) \\
\frac{dN(j_{\max})}{dt} &= k_a N_{rw} N_A (N(j_{\max}-1) + N(j_{\max})) - \frac{k_t}{v_p N_A}(j_{\max}(j_{\max}-1)N(j_{\max})) \\
&\quad -(k_{zp} Z_p + k_{de})(j_{\max} N(j_{\max}))
\end{aligned}
\tag{5.2.52}
$$

Solving these balances make it possible to calculate average number of radicals per particle (See Equation 3.4.2), and utilize this in the polymerization rate expression.

New method; Moles of radicals in the polymer particles

A new method that calculate moles of radicals in the polymer particles was derived. It is also possible to calculate number of radicals in the polymer particles with small changes in the units in the balances. This method avoids solving the radical balances dynamic. This was done to simplify the model and to give more options for getting information about the radical distribution. In the new method a steady state distribution of the radicals is utilized, so the equation set already given in Equation 5.2.52 is solved as steady state. The new method requires that moles of particles are calculated. A change in the polymerization rate expression has to be performed, as the average number of radical per particle is not calculated. Moles of radicals in the polymer particles are found instead. Moles of particles in the reactor can be both a state in this method, but it can also be an intermediate calculation. Some symbols utilized are listed below.

- N_p: Moles of particles.
- N_R: Moles of radicals .
- N_{ini}: Moles of initiator molecules.
- N_j: Moles of particles with j radicals.

A general form for the balance on the number of particles could have been utilized, but it has been decided to utilize balances which give moles of particle with j radicals, as given in Equation 5.2.53.

$$\begin{aligned}\tfrac{dN_j}{dt} &= k_a N_{rw} N_A (N_{j-1} - N_j) + \tfrac{k_t}{v_p N_A}[(j+2)(j+1)N_{j+2} - j(j-1)N_j] - \\ &(k_{de} + k_{zp} Z_p)[jN_j - (j+1)N_{j+1}] + \delta(1) r_p\end{aligned} \tag{5.2.53}$$

Total moles of radicals are given in Equation 5.2.54. This is a sum of all radicals that are on the polymer particles and the radicals that is in the water phase. Moles of radicals in the water phase will probably be small, as both termination and propagation in the water phase is not considered.

$$N_R = \sum_{j=0}^{\infty} jN_j + N_{rw} \tag{5.2.54}$$

Moles of particles and initiator is a state in this method, and these two are given in Equation 5.2.55 and 5.2.56. An expression for N_p has to be found (r_p), but it is also possible to calculate moles of particles as an intermediate calculation. There are different options here, but r_p utilized in this work will be given in Section 5.2.6.

$$\frac{dN_p}{dt} = r_p \tag{5.2.55}$$

$$\frac{dN_{ini}}{dt} = F_{I,in} - k_I N_{ini} \tag{5.2.56}$$

A total balance for the radicals and a balance for radicals in water was found, and these are given in Equation 5.2.57 and 5.2.58. Termination in water phase was not considered in either equations, as there are few radicals in the water phase compared with radicals in the polymer particles. If this is going to be considered, a new parameter is introduced in the model (k_{tw}) and a value for this is not always readily to find. From Equation 5.2.57 it can be seen that radicals are formed from decomposed initiator and radicals can only disappear because of termination. Inhibitor is also included. The total balance for the radicals can be found from the equation set given in Equation 5.2.52, and this is shown in Appendix A.6.

$$\frac{dN_R}{dt} = 2fk_I N_{ini} - \frac{2k_t}{v_p N_A} \sum_{j=0}^{\infty} (j+2)(j+1)N_{j+2} - N_R(k_{zp} Z_p + k_{zaq} Z_{aq}) \tag{5.2.57}$$

$$\begin{aligned}
&\tfrac{dN_{rw}}{dt} = 2fk_I N_{ini} - r_p - k_a N_{rw} N_A N_p + k_{de} \sum_{j=1}^{\infty} jN_j - k_{zaq} Z_{aq} N_{rw} \\
&\sum_{j=1}^{\infty} jN_j = N_R - N_{rw} \\
&\tfrac{dN_{rw}}{dt} = 2fk_I N_{ini} - r_p - k_a N_{rw} N_A N_p + k_{de}(N_R - N_{rw}) - k_{zaq} Z_{aq} N_{rw}
\end{aligned} \tag{5.2.58}$$

Moles of radicals in the water phase can be found by solving Equation 5.2.58 assuming steady state. This is given in Equation 5.2.59.

$$N_{rw} = \frac{2fk_I N_{ini} - r_p + k_{de} N_R}{k_a N_A N_p + k_{zp} Z_{zp} + k_{de}} \tag{5.2.59}$$

Moles of particles with zero radical, one radical, etc. have to be found. A dynamic equation for total number of radicals can be written on vector form as given in Equation 5.2.60, where the second term on the right hand side in Equation 5.2.57 is changed by using some matrices.

$$\frac{dN_R}{dt} = 2fk_I N_I - \frac{k_t}{v_p N_A} \underline{c}^T A^{-1} \underline{b} - (N_R(k_{zp} Z_p + k_{zaq} Z_{aq})) \tag{5.2.60}$$

where $\underline{c}^T = 2 \cdot [0, 0, 2, 6, ...(j+2)(j+1)....]$.

The radical balance that was given as a set of equations in 5.2.52 has to be solved by using matrices ($A\underline{n} = \underline{b}$) and assuming steady state. An $\widetilde{A}$ matrix is found from the radical balances and this is not a difficult task, $\underline{n}$ is a vector that gives moles of particles with zero, one, etc. radicals. An example of an A matrix when j_{max}=4 is given in 5.2.61, but inhibitor is not considered.

$$\begin{bmatrix}
-k_a N_{rw} N_A & k_{de} & \frac{2k_t}{v_p N_A} & 0 & 0 \\
k_a N_{rw} N_A & -k_a N_{rw} N_A + k_{de} & 2k_{de} & \frac{6k_t}{v_p N_A} & 0 \\
0 & k_a N_{rw} N_A & -k_a N_{rw} N_A - \frac{2k_t}{v_p N_A} + 2k_{de} & 3k_{de} & \frac{12k_t}{v_p N_A} \\
0 & 0 & k_a N_{rw} N_A & -k_a N_{rw} N_A - 3k_{de} - \frac{6k_t}{v_p N_A} & -k_a N_{rw} N_A + 4k_{de} \\
0 & 0 & 0 & k_a N_{rw} N_A & k_{de} + k_a N_{rw} N_A - \frac{12k_t}{v_p N_A}
\end{bmatrix} \tag{5.2.61}$$

This method is valid for any number of j_{max}, and this can therefore be utilized in modeling of any emulsion polymerization process independent on average number of radicals per polymer particle. This will also be programmed in MATLAB so that only j_{max} has to be specified. $\widetilde{A}$ is inverted and multiplied with b, and this give moles of particles with zero radical, one radical, two radical up to j_{max} radical per particle (see 5.2.62).

$$\widetilde{A} \begin{bmatrix} N_0 \\ N_1 \\ N_2 \\ . \\ . \\ N_{j,\max} \end{bmatrix} = \begin{bmatrix} 0 \\ r_p \\ 0 \\ . \\ . \\ 0 \end{bmatrix} \tag{5.2.62}$$

$\widetilde{A}$ is in this case singular, and det($\widetilde{A}$)=0. The first row was changed to ones, and the b matrix was changed as shown in 5.2.63. This can be done since $N_0+N_1+N_2+N_3...+N_{j,max}=N_p$.

$$A\begin{bmatrix} N_0 \\ N_1 \\ N_2 \\ . \\ . \\ N_{j,\max} \end{bmatrix} = \begin{bmatrix} N_p \\ r_p \\ 0 \\ . \\ . \\ 0 \end{bmatrix} \tag{5.2.63}$$

It is again mentioned that in this derivation, moles of particles (N_p) is a state in the model. This method will alter if moles of particles are not a state. The alteration will be in the b matrix, and the new matrices are given in 5.2.64. In this case $\sum N_j = 1$, where a standardization is used, so it is not N_p that is equal to one. Further equations given, assume that N_p is a state.

$$A\begin{bmatrix} N_0 \\ N_1 \\ N_2 \\ . \\ . \\ N_{j,\max} \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ . \\ . \\ 0 \end{bmatrix} \tag{5.2.64}$$

A new expression for polymerization rate is derived and the new expression is given in Equation 5.2.65. The units of R_p is mole/s.

$$R_p = k_p[M]_p N_p \bar{n} = k_p[M]_p N_p \frac{\sum\limits_{j=0}^{\infty} jN_j}{\sum\limits_{j=0}^{\infty} N_j} = k_p[M]_p(N_R - N_{rw}) \tag{5.2.65}$$

This method will introduce two new tuning parameters in the model. This is desorption rate and absorption rate of radicals. Desorption and absorption rate are different for the different emulsion polymerization processes. These two rate constants will have an impact on the average number of radicals per particle through the process and they are not actually constant through the batch.

Zero-one system

As the average number of radicals per particle is low for some processes i.e. PVC («0,5), a quasi-steady state calculations of the radical distribution in particles, assuming a zero-one system was derived. For processes with $\bar{n} < 0,5$, this will be the simplest method for calculation of the radical distribution. The intention of this was to make the system less stiff, and a solver with constant step length could be utilized. Assumptions made in this method are listed below.

- Number of particles with two or more radicals can be neglected, as this amount is small compared to amount of particles with zero and one radicals.

- Immediately after radical number two enters a particle, the particle chain terminate instantaneous.

When these assumptions are utilized, all polymerization that happens in particles with several radicals are not considered. Three simple balance equations for moles of particles with zero, one and two radicals can be given (See Equation 5.2.66).

$$\begin{aligned} \frac{dN_0}{dt} &= -k_a N_{rw} N_A N_0 + \frac{2k_t}{v_p N_A} N_2 + k_{de} N_1 \\ \frac{dN_1}{dt} &= k_a N_{rw} N_A (N_0 - N_1) - k_{de} N_1 + \delta(1) r_p \\ \frac{dN_2}{dt} &= k_a N_{rw} N_A N_1 - \frac{2k_t}{v_p N_A} N_2 \end{aligned} \tag{5.2.66}$$

The equations given in 5.2.66 can be solved as steady state, and after some derivation the only two equations that have to be solved are given in Equation 5.2.67. From this N_{rw} and N_1 can be found, and the new expression for the polymerization rate is given in Equation 5.2.68. The complete derivation of this is given in Appendix A.1.

$$\begin{aligned} 0 &= 2fk_i N_{Ini} - 2k_a N_{rw} N_A N_1 \\ 0 &= k_a N_{rw} N_A (N_p - 2N_1) - k_{de} N_1 \end{aligned} \tag{5.2.67}$$

$$R_p = k_p [M]_p N_1 \tag{5.2.68}$$

5.2.6 Number of particles

There are several possibilities to calculate the number of particles. It is important to remember that particles are formed in Interval I, and number of particles remains constant in Interval II and III. Particles will be given in moles in the modeling of emulsion polymerization. Other equations utilized will change dependent on the unit of N_p. First the idea was to utilize the empirical equation found by Smith-Ewart, given in Section 3.4.4 (with both upper and lower limit). The problem with this is to find an expression for the particle growth rate ($\frac{dv_p}{dt}$). It is normal in literature to set the growth rate constant, and calculation of N_p will become one more intermediate calculation in the model. If the growth rate is unknown it can be estimated, or another method to calculate moles of particles has to be found.

Moles of particles as a state is given from Equation 5.2.69. This equation introduce a new variable, a_r and $\rho_i = 2fk_I N_{ini}$. This was done to make the modeling in MATLAB more accessible. The variable a_r is given in Equation 5.2.70.

$$\begin{aligned} \frac{dN_p}{dt} &= \rho_i (1 - a_r) \ if \ a_r < 1 \\ \frac{dN_p}{dt} &= 0 \ otherwise \end{aligned} \tag{5.2.69}$$

$$a_r = \frac{N_p a_p}{a_s S} \tag{5.2.70}$$

An expression for a_p was found and this is given in Equation 5.2.71.

$$a_p = 4\pi \left(\frac{3}{4\pi} \frac{V_p}{N_p}\right)^{2/3} \tag{5.2.71}$$

The equation used to calculate moles of particles is actually a dynamic approximation to the Smith-Ewart theory given in Section 3.4.4.

5.2.7 Molecular weights

Moment balances for dead and live polymers were derived, even though they are available in different literature. Often the moment balances are given in literature, but the derivation of these balances are not given. The derivation of some of these equations are therefore given in Appendix A.2. To find the weight average molecular weight, six new states are introduced into the model. The moment equations are utilized to find molecular weight distribution, average molecular weight and polydispersity index, and this has already been explained in Section 3.4.6. The kinetic consider in derivation was initiation, propagation, termination, and chain transfer to monomer and chain transfer agent. The first step is to find balances for live radicals and dead chains of length n, accounting for all the consumption and generation terms from the kinetic mechanisms listed in Section 3.2. The species balances given in Equation 5.2.72 and 5.2.73 are utilized to find a differential equation for each moment.

$$\begin{aligned}\tfrac{dP_n}{dt} &= \{2fk_I[I] + (k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA]) \sum_{j=1}^{\infty} [P_j]\}\delta(n-1) + k_p[M]([P_{n-1}] - [P_n]) \\ &-\{k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA] + (k_{td}+k_{tc}) \sum_{j=1}^{\infty} [P_j]\}[P_n] + k_{tr}^{pol} n[D_n] \sum_{j=1}^{\infty} [P_j] - k_{tr}^{pol}[P_n] \sum_{j=1}^{\infty} j[D_j]\end{aligned} \tag{5.2.72}$$

$$\begin{aligned}\tfrac{dD_n}{dt} &= \{k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA] + k_{td} \sum_{j=1}^{\infty} [P_j]\}[P_n] + \tfrac{1}{2}k_{tc} \sum_{j=1}^{n-1} [P_j][P_{n-j}] \\ &+k_{tr}^{pol}[P_n] \sum_{j=1}^{\infty} j[D_j] - k_{tr}^{pol} n[D_n] \sum_{j=1}^{\infty} [P_j]\end{aligned} \tag{5.2.73}$$

The Kronecker delta function, $\delta(x)$, is 1 if x=0 and 0 if $x \neq 0$. This function captures the generation of new polymeric radicals, P_1. Termination by combination accounts for the possibility of creating D_n from any combination of two smaller radical fragments whose length sum to n. The species balances given in Equation 5.2.72 and 5.2.73 is substituted into the moment definitions in Equation 3.4.9 and 3.4.10. Generating functions is utilized to eliminate the tedium of performing the required series summations, and this give the following equations describing the rates of change of the moments.

Live moments:

$$\begin{aligned}\tfrac{d[\mu_0]}{dt} &= 2fk_I[I] - (k_{td}+k_{tc})[\mu_0]^2 \\[1em] \tfrac{d[\mu_1]}{dt} &= 2fk_I[I] + k_{tr}^{mon}[M][\mu_0] + k_{tr}^{CTA}[CTA][\mu_0] + k_p[M][\mu_0] - \{k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA] \\ &+(k_{td}+k_{tc})[\mu_0]\}\,[\mu_1] + k_{tr}^{pol}([\mu_0][\nu_2] - [\mu_1][\nu_1]) \\[1em] \tfrac{d[\mu_2]}{dt} &= 2fk_I[I] + k_{tr}^{mon}[M][\mu_0] + k_{tr}^{CTA}[CTA][\mu_0] + k_p[M]([\mu_0] + 2[\mu_1]) \\ &-\{k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA] + (k_{td}+k_{tc})[\mu_0]\}\,[\mu_2] \\ &+k_{tr}^{pol}([\mu_0][\nu_3] - [\mu_2][\nu_1])\end{aligned} \tag{5.2.74}$$

Dead moments:

$$\begin{aligned}
&\tfrac{d[\nu_0]}{dt} = k_{tr}^{mon}[M][\mu_0] + k_{tr}^{CTA}[CTA][\mu_0] + k_{td}[\mu_0] + \tfrac{1}{2}k_{tc}[\mu_0] \\
&\tfrac{d[\nu_1]}{dt} = k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA] + (k_{td}+k_{tc})[\mu_0][\mu_1] \\
&+k_{tr}^{pol}([\mu_1][\nu_1] + [\mu_0][\nu_2]) \qquad (5.2.75) \\
&\tfrac{d[\nu_2]}{dt} = k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA] + (k_{td}+k_{tc})[\mu_0][\mu_2] + k_{tc}[\mu_1]^2 \\
&+k_{tr}^{pol}([\mu_2][\nu_1] + [\mu_0][\nu_3])
\end{aligned}$$

As can be seen $[\mu_2]$ and $[\nu_2]$ depends on $[\nu_3]$, so these two equations suffers from a moment closure problem. There is a method that assumes that the molecular weight distribution can be represented by a truncated series of Laguerre polynomials, and this is utilized to find an approximated solution of $[\nu_3]$. This is given in Equation 5.2.76. [13]

$$[\nu_3] = \frac{[\nu_2]}{[\nu_0][\nu_1]}(2[\nu_0][\nu_2] - [\nu_1]^2) \qquad (5.2.76)$$

5.2.8 Reactor cooling

There are different cooling systems that can be utilized to cool the reactor mixture. A cooling jacket or reflux condenser is two possible solutions that are often utilized. In this work a cooling jacket was utilized and this was not divided into several sections, so an even distribution of water between the sections in the cooling jacket is assumed with the same temperature. Plug-flow in the cooling water is normal to assume in the modeling. When the cooling jacket is divided into several sections, the numbers of states in the model increase. Outlet temperature in the cooling jacket is therefore a state in the model. Inlet cooling temperature can be set constant and cooling water flow is controlled by a controller implemented in the model. It is also possible to control inlet cooling temperature, if a heat exchanger or recycling is utilized. An average temperature of the inlet and outlet cooling temperature was utilized in the energy balances. A simple illustration of a batch with a cooling jacket is given in Figure 5.1. A cooling system can also consist of both a cooling jacket and a reflux condenser. This has not been modeled or utilized further in this work, but for the interested reader this is performed in Mejdell et.al [32].

5.3 Numerical integration of the model

The mathematical dynamic model is actually a set of algebraic and differential equations (DAE). The algebraic equations (AE) in the model are possible to order so that they can be solved as intermediated calculations instead of solving a DAE equation set. A solver in MATLAB was utilized, ODE15s, as this solver is a variable-order solver for stiff systems. It is based on the numerical differentiation formulas (NDF). The NDFs are generally more efficient than the closely related family of backward differentiation formulas (BDF), also known as Gear's

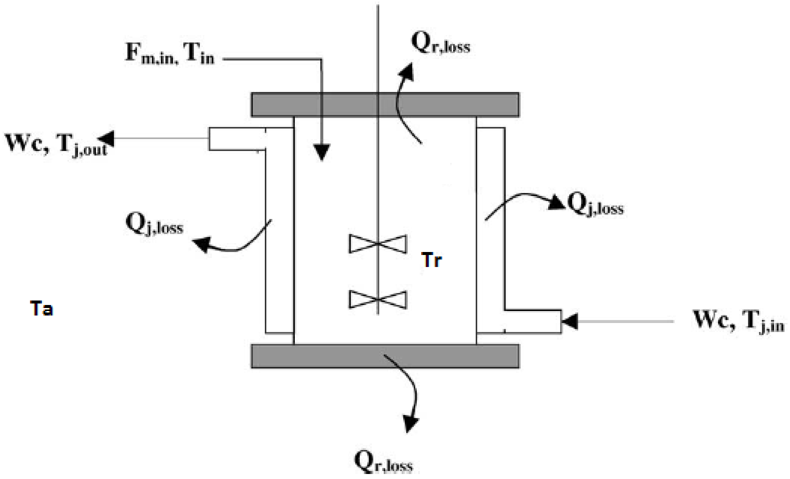

Figure 5.1: Illustration of reactor with cooling jacket [5]

method. The ODE15s properties let you choose among these formulas, as well as specifying the maximum order for the formula utilized. The solver, ODE15s, can also be utilized to solve DAE system, where only a mass matrix has to be specified. More information about ODE15s and other solvers can be found in MATLAB help function.

5.3.1 Stiff systems

The problem with stiffness is relevant to chemical engineering systems and there are methods and available solvers to solve these stiff systems (like ODE15s). In different literature stiffness has different definitions and a short explanation will only be given. Systems gets stiff when the integration step-length is restricted by the fastest transient, but the solution trajectory is determined by the slower ones [33]. A definition given is [33]:

Definition 1. *A problem is stiff if the integration step-length is restricted by stability rather than by accuracy.*

Stiffness is determined by both the mathematical model and the integration method applied to it. If slow and rapid changing processes are coupled, a stiffness problem will take place, as such processes have small and large time constants [34]. A system like this is stiff if the slow process is rate-controllable and all variables respond slowly. Rapid processes that are coupled with slow ones occur in chemical and nuclear reacting systems and in process control problem. One example is if a process has a reactor with both fast and slow reactions. Fast reactions have a small time constant and slow reactions have a large time constant. Together these two reactions give a stiff reactor system. Different efforts can be taken to eliminate stiffness problems, i.e. using an implicit integration-method with a large stability region, or algebraic equations can be solved by e.g. Newton iteration. A model simplification can also be done, and in some cases the assumption of pseudo steady-state can be utilized to eliminate the most rapid processes [33].

5.4 Discussion: Modeling

In the start of this work it was decided to model different cooling systems for the reactor. As other aspects of the process took more time than assumed, i.e. modeling of monomer distribution and radical distribution on the polymer particles, other possible cooling solutions were not considered. When modeling emulsion polymerization, decisions about how advanced the model should be have to be made in the start. The more advanced the model gets, including different aspects in the process, several more parameters have to be estimated and introduced in the model. To estimate all these parameters a broad assortment of measured process data has to be available. These measurements are in some polymerization processes secret or they are costly to perform, and some variables are actually impossible to get information about. This makes it difficult to implement complex models with several parameters in a control system. It was therefore decided to develop models that are as simple as possible, but still get satisfying predictions.

There were two energy balances, one for outlet cooling temperature and the other for reactor temperature in the model. To utilize the energy balance for the reactor temperature and achieve correct temperature a controller had to be implemented in the model. This controller should control the cooling water flow rate or the temperature of the inlet cooling water. If this was not implemented the model would not predict correct reactor temperature, as this was tested in the model. Other control systems can probably also be utilized, but independent of control configuration implemented in a plant, the controller had to be tuned. The problem by implementing a simple PI-controller was the time delay, and this would cause a problem in the simulation of the model.

By performing model reduction and simplifications, a less complex model can be obtained. Simple models that do not require a heavy computational load but capture all the essential process features are readily amenable to reactor optimization and control studies. Some aspects were therefore modeled in different ways, to make the model simpler and to reduce stiffness. As ODE15s was utilized, stiff models were not a problem and calculation time for simulating the model over a long time interval was short. A batch on 7-8 hours was simulated and this took about 8-9 seconds to calculate in MATLAB. In some cases a solver like ODE15s is not available, and therefore a solver, based on Euler, was made in MATLAB. This was tested on the model, using all the different calculation methods, where there were given different ways to calculate one variable. As the model was both complex and stiff in some cases, i.e. the extremely fast dynamic for some states, the step size h had to be quite small (about 0,0001) and this gave a calculation time around 1000 seconds. In this case h was kept constant through the whole batch simulation. Different efforts was performed to reduce the stiffness and increase h, and further reduce the calculation time. To utilize this Euler solver, with a h that gave a normal calculation time; a method like the zero-one system and steady state solution of moles of particles had to be utilized. N_p was not solved as steady state in this work, but it should be if a solver like ODE15s is not available.

There were derived and found different methods or equations to model the same variable, and this have been done for the concentration of monomer in the polymer particle and calculation of the radical distribution on the polymer particles. Simpler models were studied as these can be able to give satisfying predictions and still the model can be utilized for control purpose. It was important to have information about the monomer concentration in polymer particle as it affects the polymerization rate, and to control the process the predicted value has to be correct. The simple method derived in this work for $[M]_p$ was readily to derive, and it should give reasonable predictions. If Flory-Huggins method was utilized the model gets more comprehensive and this would also introduce some parameters that had to be estimated. The interaction parameter is important when Flory-Huggins equation is utilized, and it was calculated by using four parameters (Appendix A.7). These parameters should be adjusted by using experimental data or measured data. As measured data are often limited, the simple method was more preferred to utilize than the method using Flory-Huggins equation. Both methods should give reasonable predictions. The sub-model that utilizes Flory-Huggins equation calculates other variables that might be important in some cases. In this method the distribution of monomer in all phases was given and this could be interesting to have information about. Amount of monomer in the gas phase start to decrease in Interval III, and this would influence the pressure. Flory-Huggins method will probably give good predictions if the parameters for the interaction parameter is estimated correct for each process it is utilized on.

Moles of radicals in the polymer particles, or the average number of radicals per particle was also an important value that influences the polymerization rate. The new method calculated moles of radicals in the polymer particles, and this method should predict correct values for $N_{r,p}$. It was therefore not necessary to have moles of particles with zero, one, two etc. as states, and a number of more ODEs has to be solved. These two methods should give an approximate equal solution, but the new method was readily to utilize and understand, and in addition initial values were not needed. For some models the initial value can be important if the model is nonlinear. The zero-one system could also be a reasonable method to utilize when modeling an emulsion polymerization process, but this solution only count for processes with a low $\overline{n} < 0,5)$ average number of radicals per polymer particle. This method should reduce the stiffness in the system, and be able to predict satisfying values. How good the different sub-models are can only be verified by testing each of them on a case. This was performed in Chapter 7.

The sub-models derived were possible to utilize if different grades were modeled. Different grades can be made by using another recipe, or dosing initiator, monomer and surfactant in different ways into the reactor. In the mole balances of monomer, surfactant and initiator it was possible to post-dose but small changes had to be done in the mole balances and the programming files for the initiator and monomer. The recipe given is readily to make change in, as change in recipe only change amount of chemicals and temperature utilized. This can be done by changing amount and include new chemicals in a parameter file, which further demand for new values for heat capacities, densities, etc. Different grades can be produced if different factors in the reactor are changed, and some are listed below.

- Chain transfer agent (CTA) can be utilized to change molecular weight (MW). CTA is included in the moment balances, and a mole balance for *CTA* is given.
- Large increase in MW can be done by decreasing the polymerization rate, by lowering the initiator concentration or lowering reaction temperature. Temperature profile can be given as an input in the model or found by using an energy balance, and by controlling the flow of cooling water the temperature can readily be changed through the batch.

- The number of polymer particles (N_p) is the prime determinant of the rate and degree of polymerization. This depends on a_sS. Moles of particles also depend on rate of radical's generation. High particle numbers are associated with small particle size and low particle numbers with large particle size. Number of particles can be increased by increasing surfactant concentration in the reactor recipe.
- Utilize of inhibitor to control the polymerization. Inhibitor is included in the radical balances and a mole balance is given.

All these points listed were readily to utilize in the model. If the moment balances were utilized, this gave six new states in the model. The moment equation could be extended to include other mechanisms, such as crosslinking, reaction of terminal double bonds etc. This equation was readily to implement in reactor modeling. The disadvantage with moment equations is that these only give average quantities.

The most remarkable change that has to be performed in the sub-models is if several monomers are going to be utilized (co-polymerization). This can be time consuming, as all the modeling performed was for one monomer (mono-polymerization). It is probably not difficult to make these changes, and the sub-models given will be a good basis for this. All aspects of an emulsion polymerization process that can be useful for control purpose has not been modeled, i.e. the particle size distribution (PSD). Predictions about PSD could be utilized to determine when the batch should end.

Chapter 6

Library of configurable sub-models

In this chapter the sub-models implemented in MATLAB are given, theory and modeling for each sub-model have already been given in Chapter 5. These are given in Table 6.1 where the file name in MATLAB is given. The sub-models are made as functions and these can be called from a ”main-file”, and which sub-models that are used when modeling the process is decided from case to case. When building a model from different sub-models the structure of a complete model is readily to expand and alter. In this work the main focus has been kinetic models and polymerization with one monomer have been used for all sub-models.

6.1 Sub-models and functions in the library

There has been developed different methods to calculate different variables in an emulsion polymerization process. All these methods were programmed as sub-models in MATLAB, as this is a readily program to use where different useful functions (i.e. ODE solvers) are already available. MATLAB is also a well-known program for engineering students at NTNU. The model for emulsion polymerization is a nonlinear dynamic model, and some variables in the model make a stiff system. To solve the model, an ODE solver with variable step length that handles stiff systems was used. In MATLAB, ODE15s is the solver that can be used on stiff systems. Independent of sub-models used the model is solved as an ODE system, with intermediate calculation. A DAE-system was not necessary to use in this work.

It is normal to have reactor temperature, cooling temperature, amount of unreacted monomer, amount of initiator that has not decomposed and other chemical post-dosed in the reactor as states. In some models, other states are included depending on which sub-models used. One example is when solving the moment balances, the moment concentration for the radicals and dead polymer distribution are new states in the model. If the moment equations are going to be used, these states have to be solved with the rest of the model (*model.m*). In the library they are given in a separate file (*moment_equations.m*), but they have to be solved with other states and intermediate calculation to get a complete model. In this work the new method for calculation of radicals in the particles introduced a new state in the model, total moles of radicals. If this new method had not been used, multiple more states had to be introduced in the model, as moles of particles with zero, one, two, three, etc. radicals, have to be solved as states. The model that solve *N(j)* as states, are given in a separate model file (*model_radicals_states.m*). The zero-one-system was also programmed in a separate model file (*zero_one_system.m*). Which sub-models and models that should be utilized in modeling depend on measured process data available, because multiple parameters have to be estimated. The more measured values available, the more readily the estimation of parameters is, but measurements are not always available due to expensive measurements or impossible measurements to perform. Therefore some sub-models are not that readily to utilize if the model should be used for MPC, as lack of measured values make it difficult and sometimes impossible to estimate some parameters. Concentration of both monomer and initiator should be available, and also some information about desorption in the batch reactor and other transfer reactions. Reactor pressure, cooling flow rate and different temperatures are measurements that should always be available.

Some of the sub-models calculates variables that will be influenced if other chemicals are used, and some important chemicals are the use of inhibitor and CTA. These are normal to use in some polymerization processes, and therefore it has been included in the modeling even though it is not used in all emulsion polymerization process. The m-file *"rate_constants"* give all the different rate constants, and both rate constants for inhibitor and transfer rate constants are included. The unused rate constants are set to zero. In *"emulsion_parameter.m"* parameters can be given, and this file make it readily to change batch recipe and change the physical values for the chemicals found in different literature. The material balances for both initiator and monomer does not need a significant change to be able to model these as continuous feeds into the reactor. As the library is readily to use and expand, the model can also be used for processes where monomer is dosed in a starved condition, where this only requires some change in the mole balance for the monomer. The reactor configuration has to be known, and this includes volumes and surface areas for both the reactor and jacket. This can be calculated, as done for the case in Chapter 7, but the calculation of this is not included in this work. All sub-models are suitable to be used for modeling processes with different products grades, as this depends on how the chemicals are dosed and which chemicals used. As several more aspects could have been modeled and there are multiple different emulsion polymerization process, the work had to be limited because of time. The library is possible to develop and expand, by including both other cooling systems, change it to a continuous process, add more chemicals, etc. The most comprehensive change to make in the library is to change it to account for a co-polymerization where several monomers are used, but the library works as a good basis with a great potential for further development.

The m-files given in Table 6.1 includes both sub-models and functions with calculations needed to solve the different sub-models[1]. The matlab files utilized to esitmate the heat transfer coefficient has also been made, and included in the library. In example, calculation of monomer concentration in the polymer particles by using Flory-Huggins require saturation pressure, virial coefficients, and other calculation that have to be utilized and these were also made as functions.

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[1] All m-files that are given in Table 6.1 are in Appendix B.

Table 6.1: Library; Sub-models and other functions

	Description	File name
Main model	Use to run the model, and solves all ODEs by using ODE15s	main_model.m
Model function	Include all other sub-functions and intermediate calculations	model.m
Parameter	Process parameters are defined	emulsion_parameter.m
Rate constants	Calculate and specify rate constants	rate_constant.m
Monomer concentration $[M]_p$	A simple method for calculation of concentration of monomer in the polymer particle, and volume of polymer.	monomer_concentration_particle.m
Monomer concentration $[M]_p$	Use of partition coeff. to find monomer concentration in the polymer particle	monomer_partition.m
Monomer distribution four phases	Amount of monomer in four phases Calculate pressure, monomer concentration in the polymer particles and volume of polymer	monomer_four_phases.m
Saturation pressure	Calculate saturation pressure for monomer and water	saturation_pressure.m
Pressure Interval III	Calculate pressure in Interval III by iteration	pressure.m
Density	Calculate density of monomer, polymer and water as function of temperature	density_process.m
Virial coefficients	Find the three virial coefficients	virial_coeff.m
Polymer volume fraction	Find polymer volume fraction by iteration, for Interval II	Flory.m
Flory-Huggins interaction parameter	Calculate interaction parameter	coeffFlory.m
Activity	Calculate activity in Interval III with Flory-Huggins eq.	floryIII.m
N(j) solved as states	N(j) solved as states, with j_{max}=4	model_radicals_states.m
Radical matrix	Radical distribution in particle with new method. Find A and b matrix	radical_matrix.m
Zero-one model	Zero-one system, where all particles have zero or one radical	zero_one_system.m
Moment equations	Moment balances, PDI and MWD. Must be used with rest of the model	moment_equations.m
First part curvefit U	Define initial values, xdata and ydata to lsqcurvefit	main_curvefit_U.m
Second part curvefit U	Send in parameters that should be estimated in model	main_estimation_curvefit_ode15s.m
Third part curvefit U	The model that is solved by the second part of curvefit	estimation_U.m

Chapter 7

Case: Emulsion polymerization of poly-vinyl chloride

Global installed capacity for poly-vinyl chloride (PVC) production is currently 47.5 million tons per year and capacity and production is expected to increase in the forecast period [35]. PVC production on world basis has grown from 24.7 million tons in 2000, to 32.3 million tons in 2009. In 2020 it is expected to reach around 55.2 million tons [35]. The most utilized feedstock is natural gas, and suspension polymerization is the most widely utilized process. A small percent, around 5-10%, is PVC produced from emulsion polymerization (E-PVC). The polymerization reaction is strongly exothermic, approximately 100 kJ/mole, and efficient removal of the heat of reaction is critical for a safe and optimal operation. PVC latexes are spray-dried and milled to form fine powders and this powder is utilized in plastisols. Emulsion polymerization of PVC from vinyl-chloride monomer (VCM) was decided to utilize as a case to test the different sub-models. Process data from an E-PVC batch was given from Ineos, and these measurements have been utilized to see how good the model predictions are.

7.1 Polymerization of poly-vinyl chloride

Modeling of a PVC emulsion polymerization process is special because of different factors in the process. The first factor is chain transfer to monomer that is one of the most important and characteristic feature of vinyl chloride polymerization. A polymer chain does not transfer its radical activity to monomer directly by abstraction of a hydrogen or chlorine atom. A head-to-head addition of monomer to the growing radical is the first mechanism of the chain transfer. Chlorine radicals are formed to a limited extent and they are kinetically free. Whether the radicals resulting from chain transfer is chlorine radical or the much less water soluble radical is important for the discussion of desorption of monomer radicals from particles to the aqueous phase. The same molar mass is obtained with both emulsion and suspension routes of polymerization when carried out at the same temperature, because of the pronounced chain transfer. [14]

Common water-soluble initiator systems utilized are often persulfate. Persulfate is the initiator that is most readily to handle. Production of E-PVC consists of highly exothermic polymerization reactions, and persulfate is preferred as these reactions become more readily to control. Surfactant utilized in E-PVC are anionic emulsifiers i.e. sodium alkyl sulfonates and sodium dialkyl sulfosuccinates. The most common surfactant is sodium alkyl sulfate. To increase latex stability neutral emulsifiers are often added during or after polymerization. Emulsifiers are not only chosen for control of the particle formation and latex stability during polymerization, but for other reasons as well. [14]

One special feature of particle formation in emulsion polymerization of PVC is due to the pronounced chain transfer to monomer with subsequent desorption of monomer radicals [14]. The number of particle formed will increase due to this process. The desorbed radicals participate in particle formation. A desorption-reabsorption mechanism will occur, and this results in a decrease in the particle growth rate and again results in a decrease in the rate of micelle consumption [14]. A low number of relatively large particles can be formed by adding a small amount of emulsifier with a high CMC. Formation of new particles may be avoided by a controlled addition of surfactant during the run. Larger particles can be obtained if polymerization is started without emulsifier, but in the presence of salt and after some time particles are stabilized by careful addition of surfactant. Surfactant is therefore often utilized in the start but also post-dosed. High rates of chain transfer and a high degree of desorption of monomer radicals from the particles may lead to a low average number of radicals per particle ($\overline{n}$). This number is much less than 0.5 (Smith-Ewart case 1) and it is normal that average number of radicals per particle is 0.0005 to 0.1 [36]. At about 75% conversion the monomer disappears as a separate phase, and Interval II ends [14].

7.2 Case study

All sub-models derived in Section 5.2 were tested with the given process data from Ineos, except for the moment balances. Activation energy and frequency factor for termination and propagation was found in literature and are given in Table 7.1. This is given for a suspension polymerization of PVC, and the parameters for propagation were utilized as basis as they were altered by estimation. This was performed due to a significant variation in the values given for each parameter, in different literature. For the initiator only the half-life was found [37], and this was utilized to make an Arrhenius equation so that the initiator decomposition rate altered with temperature.

Table 7.1: Reaction kinetic parameters for PVC production [6] [7]

Variable	Value	Units
k_p	$5\cdot 10^7 \exp(-\frac{27600}{RT_R})$	[l/mole,s]
k_t	$2{k_p}^2/K_c$	[l/mole,s]
Kc	$1,0133\cdot 10^{-4}\exp(\frac{-47722}{R}(\frac{1}{T_R}-\frac{1}{333,15}))$	[l/mole,s]

Information about the initiator and surfactant will not be given as this is confidential. The reactor temperature in this case is not constant through the batch. First the mixture in the reactor is preheated before the temperature is lowered, and temperature is increased in the end to reach a higher conversion and reduce initiator amount. In this process there are possible to post-dosed chemicals, and in this case surfactant is utilized in the start and post-dosed. Both monomer and initiator are stripped off and recycled in this process, as there are probably left some monomer and initiator after ended batch time. Measured inlet cooling temperature, cooling flow rate and reactor temperature was utilized directly in the model to avoid implementing a controller in the model.

In the modeling part, a model with moment-balances was made, but as there was no information available about the transfer reactions constants the moment balances were not tested. There were neither information nor measured data to estimate these constants. The PDI for the PVC process is low and about 1-3.

The sub-models that together give the complete model of the process are comprehensive compared to measured values available in this case. This will complicate the estimation of parameters that will be performed. Measured values available were temperatures, pressure, cooling flow and conversion. The conversion given is not measured, but it is estimated by using energy balances and measured temperatures. Buffer and surfactant were modeled as water, as heat capacity and other physical values were not readily to find in literature. In Table 7.2, 7.3 and 7.4 parameters utilized in the simulation of the case are given.

To compare the predicted values with the measured values some parameters had to be estimated, and how this was performed will be explained before the results of predicted values from the model is presented.

Table 7.2: Molecular weights and reaction enthalpy [7]

Parameter	Value	Unit
Molecular weight monomer [38]	62,498	g/mole
Molecular weight water [39]	18	g/mole
Reaction enthalpy for polymerization[1]	97	kJ/mole

Table 7.3: Physical properties of polymer, monomer (VCM) and water [7]

Physical property	Substance
Density [kg/m^3]; Polymer	$10^3 e^{(0,4296-3.274\cdot 10^{-4}T)}$
Density [kg/m^3]; Monomer	$947,1-1,746(T-273,15)-(3,24\cdot 10^{-3}(T-273,15)^2)$
Density [kg/m^3]; Water	$1011-0,4484(T-273,15)$
Heat capacity[kJ/kg K]; Polymer	0,934
Heat capacity[kJ/kg K]; Monomer	$4,178(18,67+0,0758(T-273,15))/62,5$
Heat capacity[kJ/kg K]; Water	$4,02e^{(-1.5366\cdot 10^{-2}T)}$

Table 7.4: Thermodynamic properties of water and VCM [7]

	Water	VCM
Vapor pressure, P^{sat} [Pa]	$\exp(72,55-7206,7/T-7,1386\ln(T)$ $+4,046\cdot 10^{-6}T^2)$	$\exp(126,85-5760,1/T-17,914\ln(T)$ $+2,4917\cdot 10^{-6}T^2)$
Accentric factor, ω	0,3342	0,1048
Critical temperature T_c [K]	647,5	432
Critical pressure P_c [bar]	220,5	56
Critical volume V_c [cm^3/mole]	56	179
Critical compressibility factor, Z_c	0,233	0,283

7.2.1 Parameter estimation

Nonlinear dynamic models derived from principles of physics and chemistry often contain parameters, and the value on these parameters cannot be accurately predicted from theory. The problem with parameter estimation is to fit a model to a set of real process measurements. In some cases parameters are difficult to determine even with highly specialized laboratory experiments and often only a subset of the parameters can be estimated due to restrictions imposed by the model structure and which process measurements that are given. To generate data well suited for estimating unknown parameters, systematic design of experiments has to be performed, and this is an important research area. In chemical plants, designed experiments are often impractical due to manufacturing constraints on product quality and throughput. A result of this is development of parameter-estimation techniques, which utilize readily available plant data. [40]

In off-line parameter estimation a model is fitted ”optimally” to the process measurements from one or multiple completed process runs. Off-line parameter-estimation problems are often formulated as an optimization problem. Unknown parameters are the decision variables and the least-square difference between measured values and model predictions are minimized, subject to constraints imposed by the model equations and known bounds on the parameters. In on-line parameter estimation a model is fitted optimally to past and present process measurements while the process is in operation. There are different available methods for on-line parameters estimation i.e. parameter estimation via state estimation, prediction-error-based estimation, parameter estimation via on-line optimization etc. [41].

Parameter estimation in MATLAB

In this case off-line parameter-estimation was performed, as some measured values were available. The rate constant for absorption, desorption and the heat transfer coefficient had to be estimated. First trial performed on parameter estimation was to find these three parameters by using *lsqcurvefit* in MATLAB. This is a part of the Optimization toolbox in Matlab. *Lsqcurvefit* solves nonlinear curve-fitting (data-fitting) problems in least-squares sense and find coefficients x that solves the problem given in Equation 7.2.1 [2].

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[2] For more information about *lsqcurvefit*, it is recommended to utilize the MATLAB help function. There is information available and examples on how *lsqcurvefit* works [42]

$$\min_x \|F(x, x_{data}) - y_{data}\|_2^2 = \min_x \sum_i (F(x, x_{data,i}) - y_{data,i})^2 \tag{7.2.1}$$

It was decided to separate the estimation into two different parts. First the heat transfer coefficient was estimated where only the energy balance for the outlet cooling temperature was utilized, as measured inlet cooling temperature and reactor temperature were utilized directly in the model. Second the kinetic parameters were estimated, and the whole model was utilized in this case with energy balances, mole balances and intermediate calculations.

Estimation of heat transfer coefficient

From the energy balances it can be seen that the heat transfer coefficient (U) has to be estimated, as both the heat transfer coefficients to the environment U_a and from the reactor top U_t were set to small values. These two are small compared to the heat transfer between the jacket and the reactor, and it was decided to set U_a and U_t equal to 25 W/m^2,K. The heat transfer coefficient (U) is not constant and will alter through the batch. The alteration in U depends on the reactor solution viscosity, and as this is unknown and not modeled another solution had to be found. Heat transfer coefficient was found by expressing this as a function of conversion. Three possible solutions to estimate U were tested for this case. The first solution was to estimate U as a constant value, p_1, the second solution was to make a linear polynomial given as $U = p_1 + p_2 X$, the last solution was to make a quadratic polynomial given as $U = p_1 + p_2 X + p_3 X^2$. Measured inlet cooling jacket temperature and reactor temperature were utilized, and the energy balance for the outlet temperature of the cooling jacket was utilized (see Equation 7.2.2). In this equation, T_{ave} is the average temperature between inlet and outlet cooling jacket temperature.

$$\frac{dT_{j,out}}{dt} = \frac{W_c c_{pw}(T_{j,in} - T_{j,out}) + U_a A_a (T_a - T_{j,out}) + UA(T_R - T_{ave})}{(m_w c_{pw} + m_m c_{pmet})} \tag{7.2.2}$$

All three possible solutions gave acceptable results when *lsqcurvefit* in MATLAB was utilized. The estimated values are given in Table 7.5. The difference between predicted and measured values of the outlet cooling temperature is given in Figure 7.1 for solution one and three. Figure 7.2 shows the temperature difference between outlet cooling temperature and inlet cooling temperature, for both measured and predicted outlet cooling temperature.

Table 7.5: Estimated parameters from *lsqcurvefit*

Solution	Value p_1	Value p_2	Value p_3
1) Constant U	388	-	-
2) Linear polynomial	450	-150	-
3) Quadratic polynomial	516	-538	426

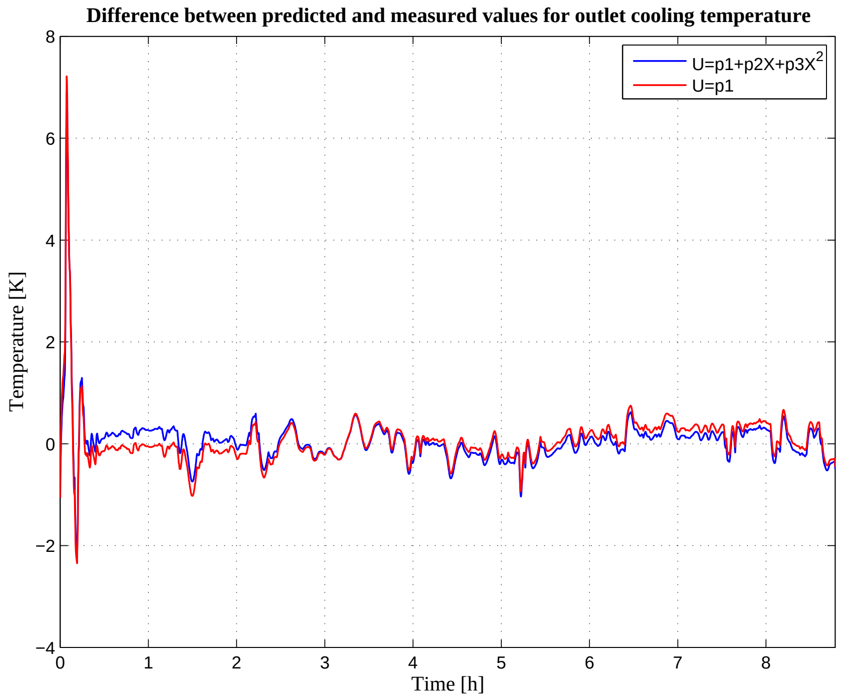

Figure 7.1: Difference between predicted and measured values of the outlet cooling temperature. The heat transfer coefficient given as a constant and expressed with a quadratic polynomial.

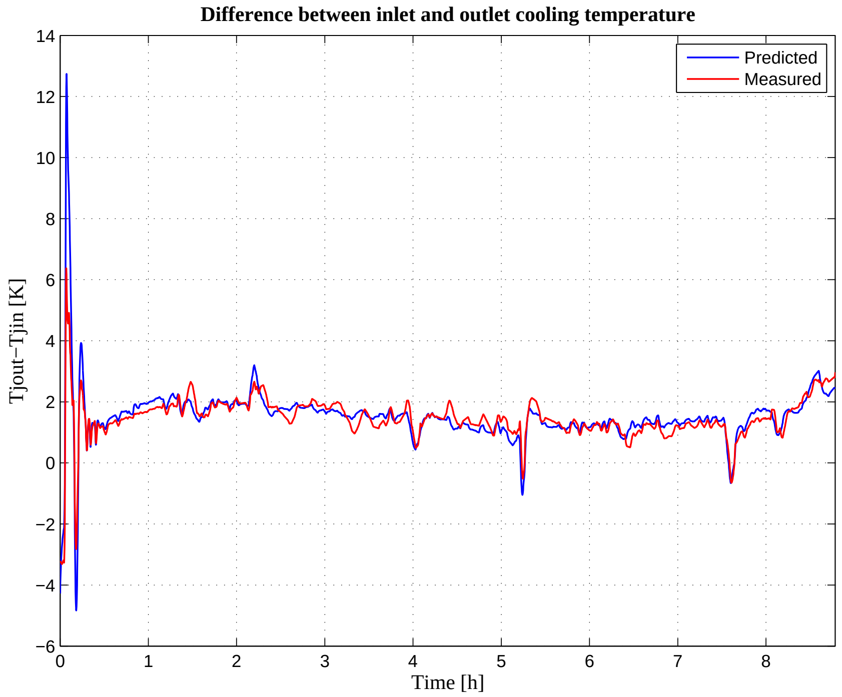

Figure 7.2: Difference between outlet and inlet cooling temperature, for both predicted and measured outlet cooling temperature

Estimation of kinetic rate constants

Propagation rate constant found in literature, which is calculated from activation energy and frequency factor by using Arrhenius equation, seemed unreliable as the activation energy was disquieting low in some literature. Parameters found in literature were different and after some research values for suspension polymerization of PVC were found. These values were decided to utilize as a basis. The case given has a significant change in the reactor temperature through the batch and the propagation rate should be sensitive to alteration in temperature. Some tuning was therefore performed on the propagation rate constant given for a reference temperature and propagation activation energy. After a reasonable Arrhenius expression was found for propagation rate, this expression was held constant independent on sub-models, recipe and measured batch data utilized in the model.

Lsqcurvefit gave acceptable results for estimation of parameters utilized to find U as a function of conversion or to keep it constant, and therefore it was also tested for estimation of kinetic rate constants. The optimization problem in this estimation is non-convex due to the nonlinear model equations, and the algorithm will probably find different local minimums. It is therefore not guaranteed that it will converge to a global minimum for this parameter estimation. Desorption rate and absorption rate constants was attempted to be estimated by using *lsqcurvefit*, but lack of measured process data made this a difficult task. Independent of which measured data utilized it converged to a minimum that could not be utilized, or it did not converge. After many attempts, it was decided that the kinetic rate constant could not be estimated with this method. A constant value for absorption rate was set, and it was decided to estimate desorption rate with trial-and-error. As this value alters through the batch, it was decided to find this rate as a function of conversion. Desorption rate actually alter with both temperature and size of particles. If several batch measurements were available this could have been used to find how the desorption rate change with temperature, but this was not possible to perform in this work. Estimation of an expression that give desorption rate as function of conversion was a simple attempt for estimation of this kinetic rate constant. Desorption rate was estimated such that predicted and given conversion had an acceptable fit through the whole batch. In Table 7.6 reaction kinetic parameters estimated and utilized in the model are given.

Table 7.6: Reaction kinetic parameters found from parameter estimation, and utilized in the simulation

Variable	Value
k$_p$	$k_p = 52725\exp(\frac{-60000}{R}(\frac{1}{T_R} - \frac{1}{323.15}))$
k$_t$	As in table 7.1
k$_{de}$	In start: 800 From X=0,005: $(5,189 \cdot 10^4 X^5) - (1,513 \cdot 10^5 X^4) + (1,553 \cdot 10^5 X^3) - (6,02 \cdot 10^4 X^2) + (1352X) + 3010$

Figure 7.3 give desorption rate as a function of monomer conversion through the batch. The desorption rate was kept low in the start, as too large desorption rate gave problems in the model. The value of k_{de} in the start of the model can be influenced by other dynamic in the model.

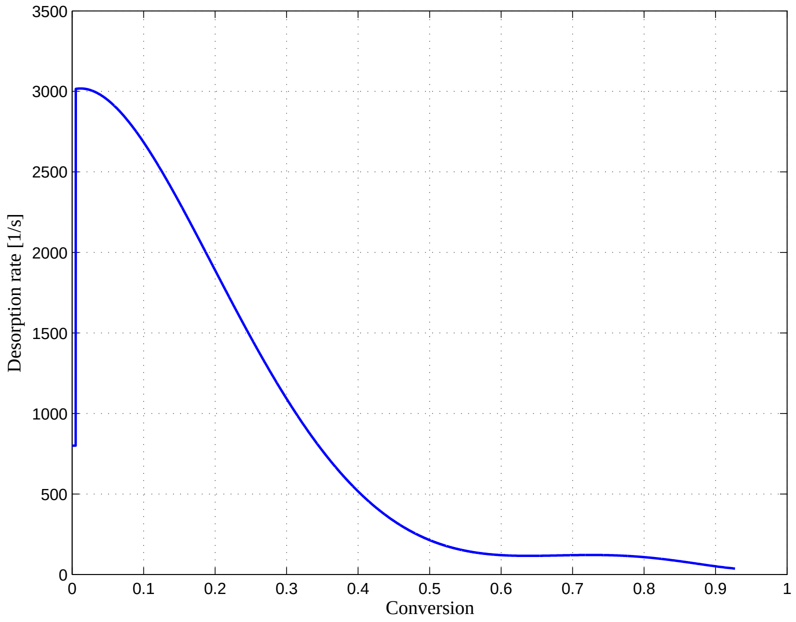

Figure 7.3: Desorption rate as a function of monomer conversion through one batch

7.2.2 Results; Model predictions

Model predictions of emulsion polymerization of PVC will be given in this section. All m-files in the library will be tested in this case. Some measured values were available, and these will be compared with the predicted values. One batch was decided to be utilized to give the results and perform the estimation on parameters, and another batch with a different temperature and recipe was tested to validate the model.

Amount of monomer in the polymer particles

This result will first be presented as two methods were utilized to calculate monomer concentration in the polymer particles through the batch. Polymerization rate depends on this value, so $[M]_p$ is an important variable. The first method was the simple method derived in this work, and the second method was the more comprehensive method that uses Flory-Huggins equation (called Flory-Huggins method). The partition coefficient method could not be utilized in this case, as the partition coefficients for this process were not available. The simple method requires that the critical conversion (x_c) is known. In this case the critical conversion was found from measured data. It was found when the measured reactor pressure became lower than the saturation pressure of VCM, for a given reactor temperature. The conversion given from Ineos was utilized as the critical conversion in this point. There can be some uncertainty in this value, as given conversion was not a measurement.

The critical conversion was found to be 0,77, and this was utilized in the model. The first plot in Figure 7.4 shows monomer concentration in the polymer particles for both methods utilized. There was a deviation between these two methods. The simple method had constant $[M]_p$ in Interval II, but it started to decrease when Interval III was reached. For Flory-Huggins method $[M]_p$ was not constant in Interval II, and started to increase right before Interval III and started to drop when conversion was approximately 0.79.

Flory-Huggins method calculated the critical conversion to be about 0,79, and this was also utilized in the simple method shown in the last plot in Figure 7.4. Monomer concentration in the polymer particles was approximately the same for these two methods in the start, but the difference between these methods increased when temperature was altered in the reactor. Calculation of the polymer volume fraction in the polymer rich phase (φ_p) depends on an interaction parameter for Flory-Huggins method. The interaction parameter will affect the critical conversion in this method and it depends on temperature. In addition, the monomer concentration will vary with alternating temperature. After approximately 3 hours the temperature and $[M]_p$ decreased for Flory-Huggins method. After approximately 8 hours the temperature and $[M]_p$ increased before the critical conversion (x_c=0,79) was reached and $[M]_p$ started to decrease when Interval III was reached.

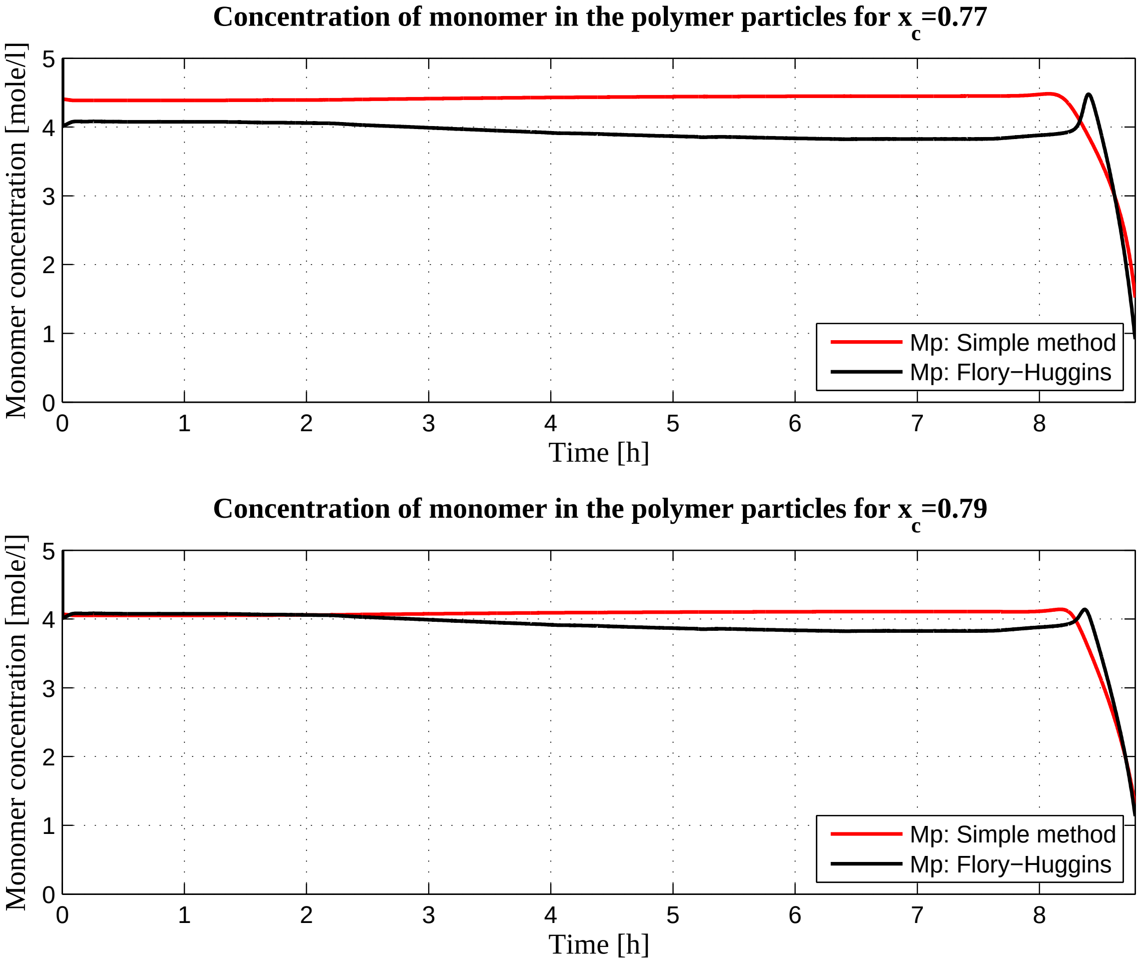

Figure 7.4: Concentration of monomer in the polymer particles

All results given further is for x_c=0,77 where the simple method for calculation of monomer concentration in the polymer particle is utilized. The new method that calculate moles of radicals in the polymer particles has been utilized in the model for the results given.

In Figure 7.5 the amount of monomer in water phase, gas phase, monomer droplets and the polymer particles (polymer rich phase) are given. As already mentioned the parameters utilized to calculate the interaction parameter should have been estimated, or the values should have been found by experiments. Interval I was implemented in Interval II in these calculations, as Interval I was short. The calculation of monomer in gas and water phase was based on pressure, and therefore the amount of VCM in the gas and water phase were not equal to zero when *t=0* in the simulation. When the simulation started there had already been established a pressure that was approximately 10 bars. The figure shows that when Interval III was reached there was a rapid decrease of monomer in the gas phase. The predicted dynamic was probably too rapid compared with the real process. Amount of monomer increased in the water phase, as the temperature increased and more monomer were dissolved in the water phase. The monomer droplets (monomer phase) does only exist up to the critical conversion, and this is also shown in Figure 7.5. This phase disappeared when the critical conversion was reached and there were no continuous transfer of monomer into the polymer particles, and the monomer concentration in the polymer particles started to decrease as the model predicted.

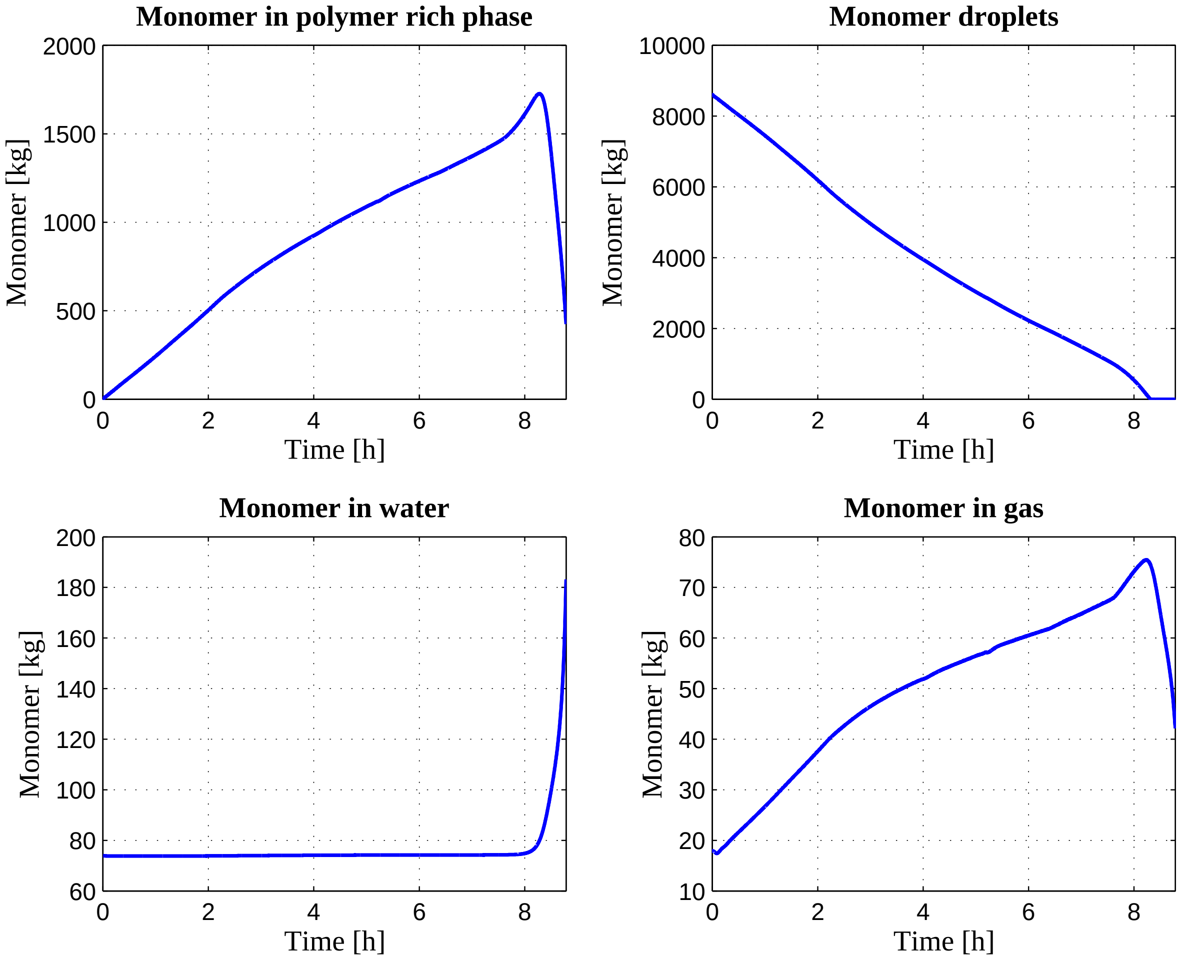

Figure 7.5: Amount of monomer in the water, gas, monomer-rich and polymer-rich phase

Temperatures

Reactor temperature in the model was the measured temperature, and this was utilized because it was difficult to compare predicted values with measured values if the reactor temperature profile was different. The energy balance that gave reactor temperature as a state was first utilized, and a PI-controller was implemented in the model and tuned. The simple PI-controller was not easy to tune, but acceptable tuning parameters were found. The PI-controller utilized the inlet cooling temperature as manipulated variable, as this is used in some processes. This gave a reactor temperature close to the measured temperature but some problems arised because of time-delay in the controller. The predicted reactor temperature got a delay compared to measured temperature, and because of this measured reactor temperature, cooling flow rate and inlet cooling temperature were utilized directly in the model to calculate the rest of the model calculations. The outlet cooling temperature is a state and predicted outlet cooling temperature (blue color in Figure 7.6) match the measured because the heat transfer coefficient U was estimated (See Section 7.2.1). There were only approximately 1-2 K in difference between measured inlet and outlet cooling temperature, and this can be seen in Figure 7.6.

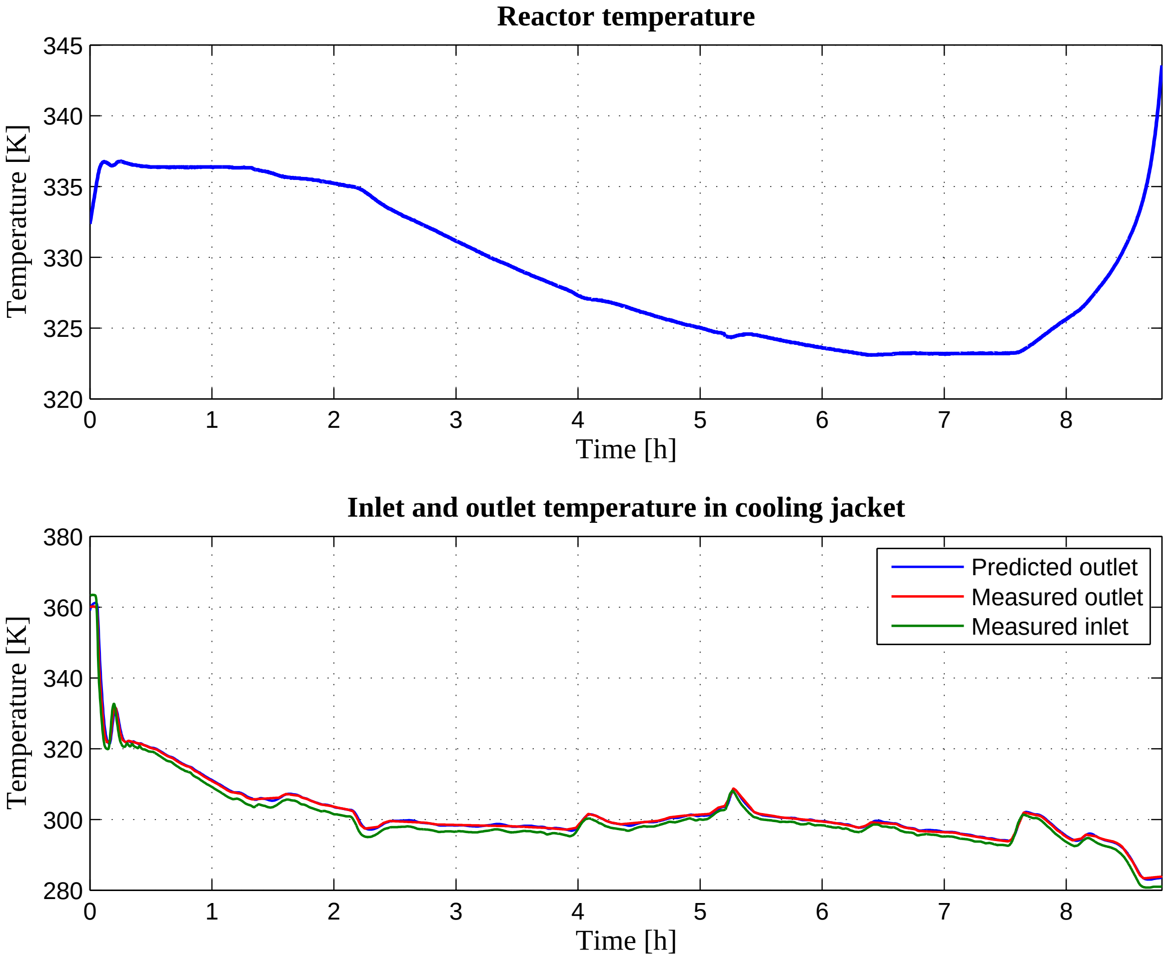

Figure 7.6: Measured reactor, inlet cooling and outlet cooling temperature, and the predicted outlet cooling jacket temperature.

Polymerization rate, conversion, moles of particles and average number of radicals per particle

In this part of the case, more concentration measurements of the different substances would have been useful for comparison. To match the predicted values with the given values for conversion, an expression for desorption rate as a function of conversion was found by estimation. The given and predicted conversion had an acceptable match, and this can be seen in Figure 7.7. It was a deviation in the start, but measured values given for conversion were negative in the start of the batch (the first minutes). This could be because of different reasons, but most probably by inaccuracy or disturbances in the measurements as conversion were actually calculated from the energy balances. The model does not predict unphysical values.

Initiator decomposes and produce radicals, and as can be seen in Figure 7.7 there was a large amount initiator left with ended batch time. From the half-life found in literature this amount should be acceptable as initiator had long half-life for most of the reactor temperatures utilized in this case. The efficiency factor (f) for the initiator was unknown, and as this is never 100% it was decided to utilize f=70%. Unfortunately there was not much information available about the initiator, and two half-life's found in literature had to be trusted.

Number of particles were predicted by the model and to control that this value was correct, a control calculation was performed. The final size of the particles was known and final conversion was given and this was utilized to calculate number of particles or moles of particles. The value calculated was approximately 0.00209 moles of particles. The nucleation stage constitutes Interval I, and the initial period in which the particle number is changing. As can be seen in Figure 7.7 for the plot of moles of particles is that Interval I was extremely short. It cannot be seen from the figure, but it lasts about 60-80 seconds. After Interval I was finished moles of particles remained constant through the rest of the batch. The model predict moles of particles to be approximately 0.002, but the value utilized for the desorption rate in the start was important in the model.

The polymerization rate depends on different variables. Figure 7.7 shows that the polymerization rate depends on reactor temperature and polymerization rate increased with increasing temperature. As the case was based on a batch reactor with alterations in the temperature, the polymerization rate was not readily to compare with literature, as given in Section 3.3. It was not possible to utilize the predicted values of the polymerization rate to see where the different intervals occur. The average number of radicals per particles was found in literature to be low for emulsion polymerization of PVC (0.0005 to 0.1). Figure 7.7 shows these values through the batch, and the average number of radicals per particle depends on temperature.

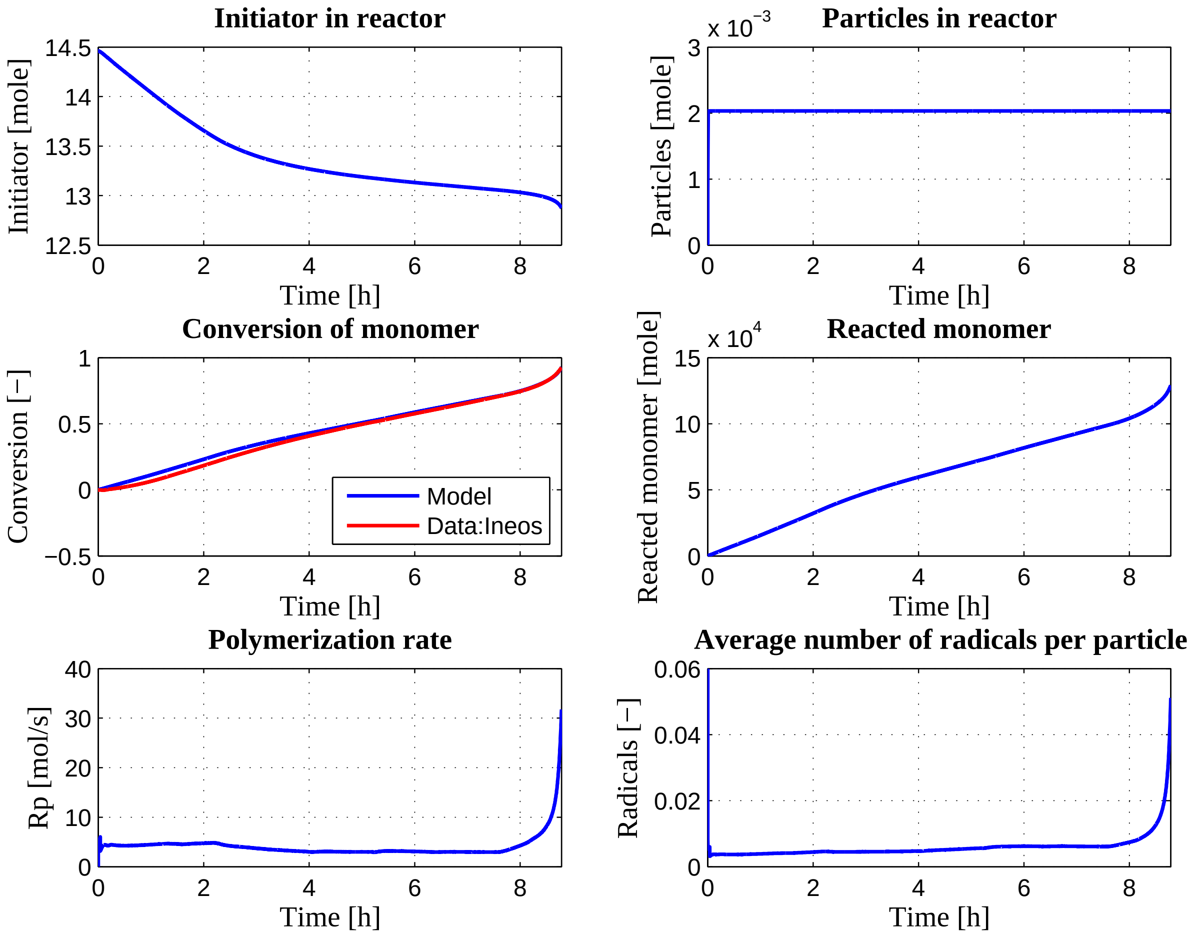

Figure 7.7: Model predictions; Initiator left, moles of particles in reactor, conversion, reacted monomer, polymerization rate and average number of radicals per polymer particle.

Reactor pressure

Pressure was calculated from both the simple method for calculations of $[M]_p$ and the thermodynamic approach where Flory-Huggins equation was utilized. In Interval I and II, reactor pressure was equal to the sum of VCM and water vapor partial pressures, assuming that the water vapor partial pressure was equal to its saturation value. In Interval III the pressure was calculated from Equation 5.2.40 for the thermodynamic approach, where this equation was solved with an iteration and activity (α_m) was found from Flory-Huggins equation. The simple method calculate pressure from $P = \alpha_m P_{sat}$ and α_m was found from Equation 5.2.34. Figure 7.8 give the predicted pressure from the simple method and the more comprehensive method, and the measured pressure and VCM saturation pressure.

The predicted pressure was close to the measured pressure in the reactor in Interval I and II. There was a small deviation in these two intervals and this can be a result of measurement noise and some uncertainty in the parameters utilized to calculate the saturation pressure. After approximately 7,6 hours, measured pressure start to increase, which is the result of increasing reactor temperature. A pressure drop was expected when reaching Interval III for the real processes, but there is a significant temperature increase and the resulting total pressure will not drop. In the real reactor there is a pressure drop when the total pressure is lower than the saturation pressure, but the total reactor pressure will not start to drop. As can be seen from Figure 7.8, the predicted pressure experienced a pressure drop after about 8,2 hours, as Interval III was reached. This results in a deviation between predicted and measured pressure in Interval III. Predicted pressure from the simple method dropped before the predicted pressure for the more comprehensive method. This was because the simple method utilize x_c=0,77 but the other method calculated this to be about 0,79. It was a deviation in the predicted pressure for these two methods in Interval III. In Figure 7.8 it is possible to observe when Interval III is reached in the real processes, as the saturation pressure of VCM become lower than the reactor pressure.

The pressure deviation in interval III, can occur from different reasons. There can be lack of some dynamic in the model that give this deviation, as in Interval III the concentration of monomer in the gas phase will start to change. Another possible reason could be that there are some uncertainties in the conversion given from Ineos. In Figure 7.9 the monomer activity is given from two calculations. The first calculation utilized Equation 5.2.34, and critical conversion was set to be 0,77 as found. The second calculation divided the saturation pressure on the measured pressure. Figure 7.9 shows where the real pressure drop occurs compared with the pressure drop in the model.

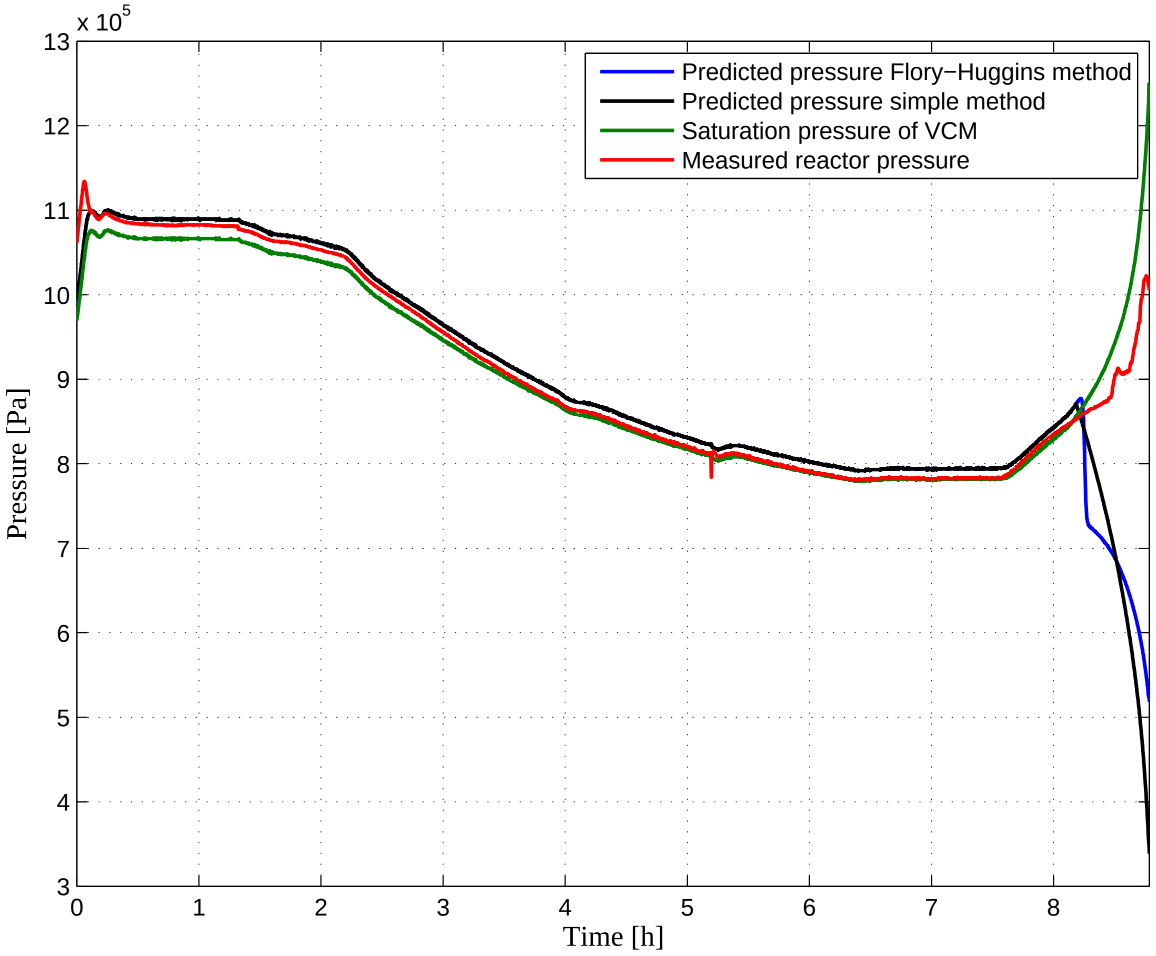

Figure 7.8: Predicted and measured reactor pressure, and saturation pressure of VCM.

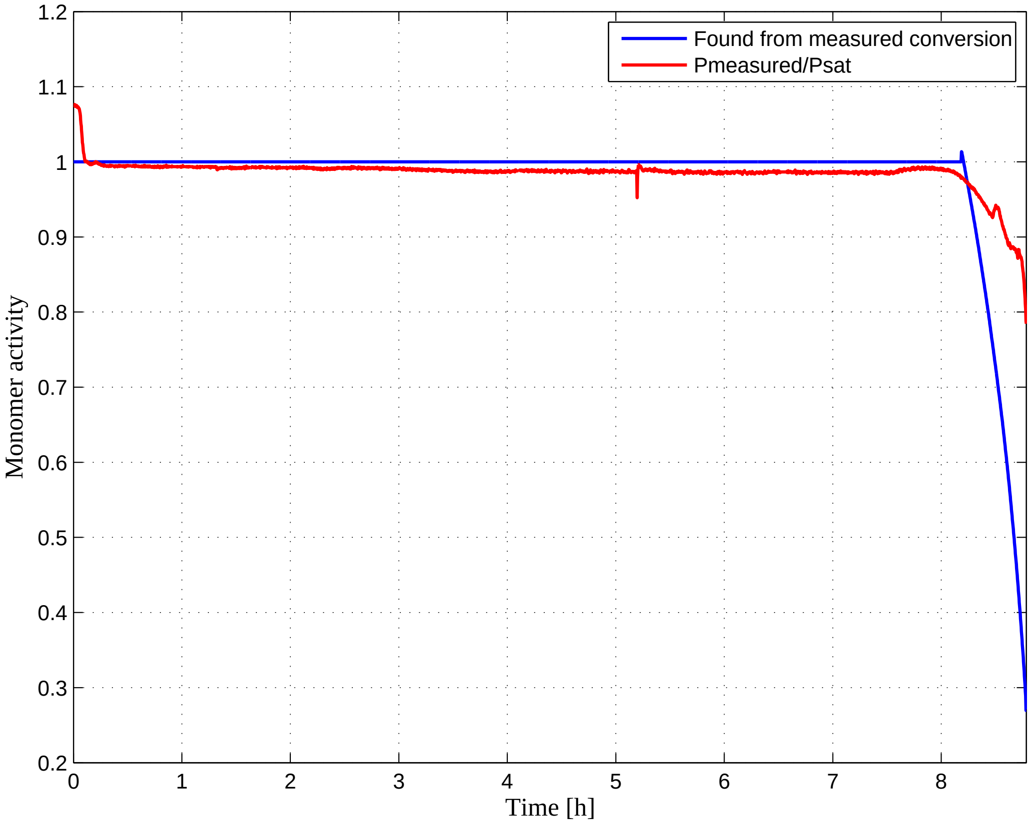

Figure 7.9: Monomer activity (α_m) calculated from given conversion ($x_c = 0,77$) and calculated from the measured pressure divided on saturation pressure

Comparing two methods to calculate distribution of radicals on the polymer particles

The new method for calculation of moles of radicals in the polymer particles has been utilized to give the results in this work. To validate this method, a model with *N(j)* as states was solved, where moles of particles with zero to four radicals per particles were utilized. Initial values had to be given and the calculation of N_p had to be altered. As *N(j)* were states, these will sum up to give N_p, and a method for calculating N_p was not needed. Both methods were therefore simulated and the results are given in Figure 7.10. The simple method for calculation of monomer concentration in the polymer particles was utilized and all parameters estimated were kept as already given above. These two methods predicted approximately the same results, with an acceptable deviation in conversion that influence $[M]_p$. This strengthens the new method for calculation of radicals in the polymer particles derived. Both methods deviate from the measured values of conversion in the start of the batch.

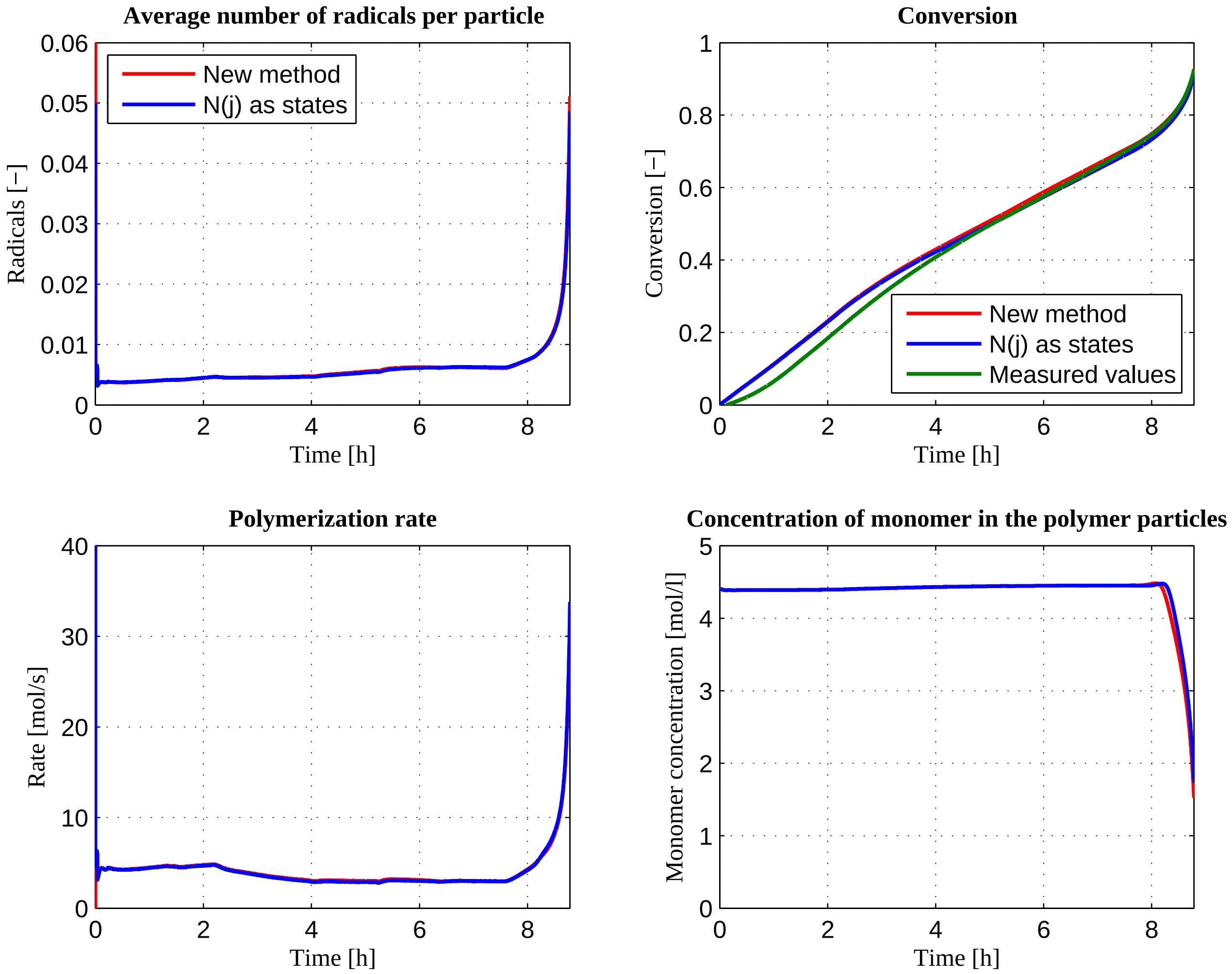

Figure 7.10: Comparing two methods to calculate distribution of radicals on the polymer particles: N(j) as states and the new method

Validation of the model; New batch data and recipe

Parameters estimated and utilized in the results shown above were kept constant, but measured values for another batch were utilized. The batch the new measured values were taken from had different properties due to another chemical composition and temperature profile. Only one parameter was altered; the desorption rate constant. The value utilized for this batch is given in Table 7.7. If the desorption rate was not altered, a good fit was experienced. Still, in order to optimize the fit; the desorption rate function was slightly altered. The results from this new batch are given in Figure 7.11. The results given in this figure utilize the simple method to calculate $[M]_p$ and the new method to find moles of radicals in the polymer particles. Measured reactor temperature, cooling flow rate and inlet cooling temperature were also utilized directly in the model for this batch.

Table 7.7: Validation of model: Desorption rate constant for a new batch

Variable	Value
k_{de}	In start: 800 From X=0,005: $(5189 \cdot 10^4 X^5) - (1513 \cdot 10^5 X^4) + (1553 \cdot 10^5 X^3) - (602 \cdot 10^4 X^2) + (1352X) + 3020$

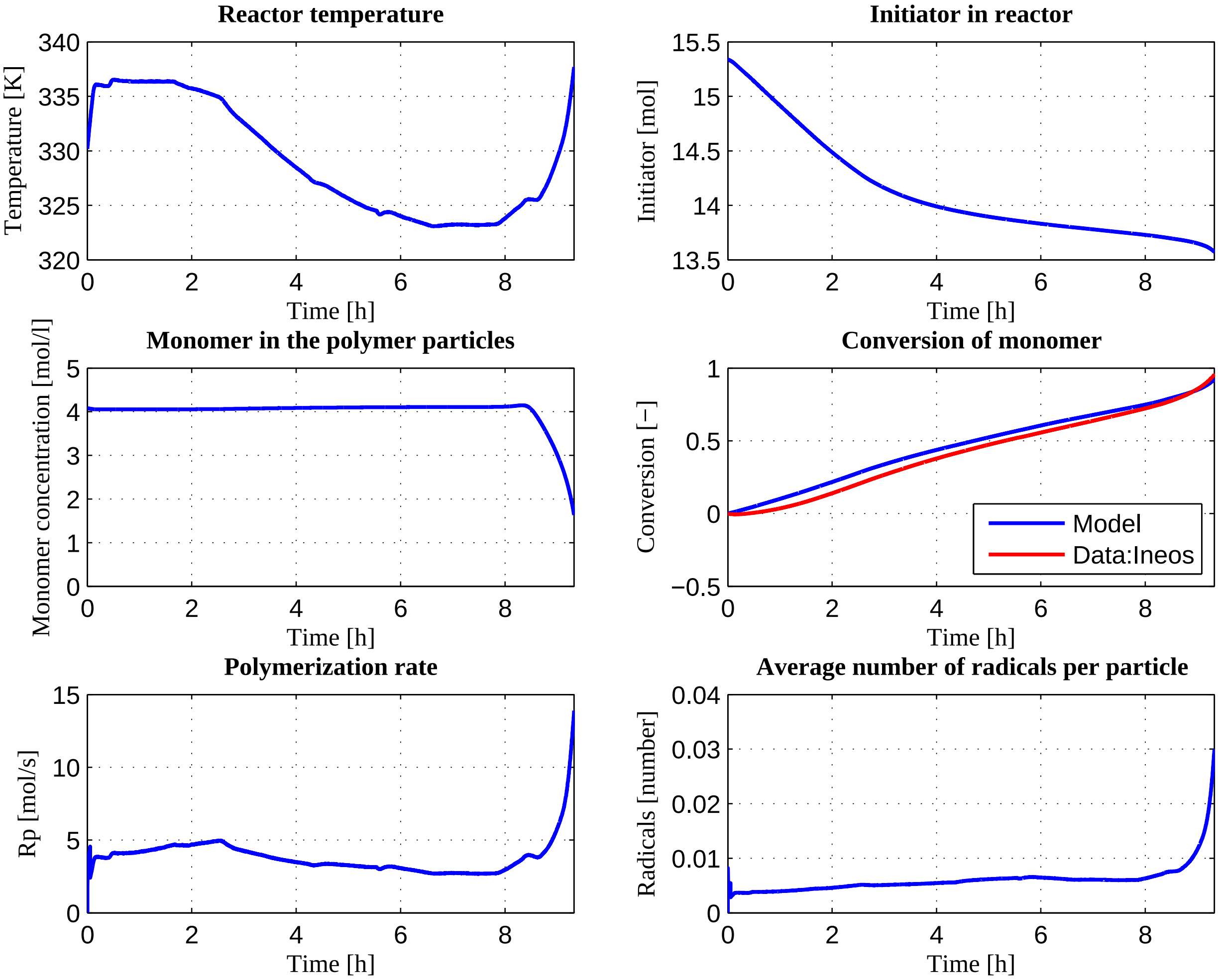

Figure 7.11: Validation of the model; model predictions when a new batch is utilized, with different recipe and temperature profile. Temperature profile and predicted values are given.

7.3 Discussion: Estimation of parameters and case results

To simulate the model and compare this with measured values from the case, some parameters had to be estimated. The estimation of all parameters was a challenging task and therefore only a few parameters were selected to be estimated. In fact other parameters should have been estimated, i.e. *a*, *b*, *c* and *d* for the Flory-Huggins interaction parameter, but this was impossible as the model is more comprehensive than measured data available. Estimation of parameters in a model, will capture mistakes and other uncertainties in the model and improve match between predicted and measured values.

As measured reactor, cooling inlet and cooling outlet temperatures were available, it was not difficult to estimate the heat transfer coefficient as a function of conversion or as a constant. The results were acceptable, and *lsqcurvefit* converged rapid to a solution. *Lsqcurvefit* was suited for this purpose. In this case the heat transfer coefficient expressed as a function of conversion was utilized, but the constant value could also be utilized. The difference between outlet and inlet cooling temperature gave some deviation for the measured and predicted values. There were measurement noise in the measurements, and it was impossible to make the predictions equal to the measured values. The predicted temperature difference in the cooling jacket follows the measured differences with an acceptable deviation. An acceptable match was achieved between predicted and measured outlet cooling temperature through the batch.

The kinetic rate constants for propagation, absorption and desorption were not readily to estimate. This also includes the rate constants for transfer to monomer, polymer, etc. and the moment's balances could not be tested in this case. It was decided to estimate kinetic parameters with trial-and-error method, as *lsqcurvefit* could not find a global minimum when these parameters were estimated. When mistakes were discovered in the model, these parameters had to be estimated all over again, which was time consuming.

Propagation rate was altered by using literature values as a basis. An advice from people knowing this field was to utilize newly published values as these are more reliable. The reason for changing propagation rate constant was that values given in literature seemed unreliable. It was found different literature on the same process, but the values given were often dissimilar. A correct activation energy that is sensitive to temperature is important in this case, as the temperature alter through the batch. As it was difficult to find reliable values for the activation energy and the frequency factor, the ones found in literature was altered. Propagation rate should have been found by experiments for E-PVC. Both propagation and termination rate constant depends on activation energy, and should actually not be estimated as these are specific for every system. Each reaction has an energy it has to reach for the reaction to occur. Due to lack of information, a simple solution had to be utilized. The value utilized in simulation was in the range of the values given in different literature.

Desorption rate was also important in this case, as this influence number of radicals per particle, and further influence the polymerization rate. In a real process desorption rate alter through the batch, because both temperature and particle size alters. It becomes more difficult for a radical to desorb from the particle when the particle is large in size. First *lsqcurvefit* was utilized to estimate a constant desorption rate, but *lsqcurvefit* found only several local minimums that were not usable. It was decided to estimate desorption rate as a function of conversion and this gave acceptable results. In the start desorption rate could not be set too large, as this caused problems in the model, perhaps because a too high desorption rate would prevent particle formation. The desorption rate was set low in the start before it increase as more particles are created and initiator has decomposed. Desorption rate decrease as the particles grow and conversion increase in the reactor. It would probably be more correct to include alteration in desorption dependent on temperature, this was tested but no usable expressions were found. It was observed in the model that when the desorption rate goes toward zero, then $\bar{n}$ goes toward 0,5, and when desorption rate increase to a high value, $\bar{n}$ get close to zero. This is logical and it was expected that the model would predict this.

After parameter estimation was performed, the model could be simulated and compared with measured process data and literature values. It should be mentioned that measured values available, which could be utilized for comparing, was temperature, pressures and conversion. Concentration measurements were not given, but it had been preferred to have both concentration measurements of monomer and initiator.

The model predicts expected values and there was a reasonable fit between predicted and measured conversion and outlet cooling temperature. There was a deviation in the beginning between predicted and given conversion. Values for the given conversion are negative in the beginning. The model does not predict negative values, which is correct as the conversion is never negative. Pressure was calculated from two different equations. The equation in Flory-Huggins method that was solved with iteration, increased the calculation time from 10 seconds to 130 seconds. *Fsolve* in MATLAB should not be utilized to solve this iteration. The predicted pressure had an acceptable match with measured pressure, except from deviation in Interval III. Measured reactor pressure increased due to a significant temperature increase, however; the model predicted a pressure drop. This deviation can occur because of different reasons and some of the theories behind the deviation can be given. Pressure was in one method calculated with the use of Flory-Huggins equation, which is dependent on some parameters. These parameters were not estimated and they will influence the calculated value for the activity, whereas activity is further utilized in the calculation of fugacity and pressure. This was a probable solution for the deviation between the two equations utilized to calculate the pressure in Interval III, but not the deviation between the predicted and measure pressure in Interval III.

A reason for the deviation between predicted and measured pressure can be the lack of dynamic in the model. When Interval III was reached the model predicted that monomer was transported rapidly from gas phase to liquid phase. In the real process, monomer in gas phase is most likely not transported into the liquid phase with the rapid dynamic that the model predicts. A theory is that transport of monomer from gas phase to liquid phase is slowed if the reactor cooling is stopped. The cooling is probably stopped to achieve the temperature increase. As a result, monomer may not start to condensate on the reactor walls and will therefore not be transported into liquid phase. Amount of monomer in gas phase will decrease remarkably slow, and the time before monomer in gas phase enters the liquid phase will be considerably longer than predicted by the model. Some dynamic could have been included in the model, i.e. a time constant. This time constant will decide how rapid monomer diffuses between different phases. Another problem found in this case was uncertainty in the conversion profile given by Ineos. The real process reach Interval III prior to the critical conversion found from given conversion and monomer saturation pressure. The critical conversion was most likely incorrect in this case. The desorption rate was estimated to give a reasonable fit between predicted and given conversion. More uncertainties may have been introduced in the model by this estimation. The correct critical conversion could not be found and measured values were trusted and utilized in this case. If the model is utilized on a process with pressure control, the model should be altered so predicted pressure in Interval III becomes correct. There would be a possibility to obtain more information about the pressure deviation in Interval III if the model was tested on a case where the reactor temperature is constant. Problems and deviation in the model was more difficult to understand when there were numerous variables that experience significant change due to the alteration in the temperature.

Two methods were utilized to calculate monomer concentration in the polymer particles. The simple method seemed to give reasonable results, even though no information about $[M]_p$ was available from the real process. Flory-Huggins method calculated a lower value for $[M]_p$ when x_c=0,77 was utilized, and this is probably because the parameters were not estimated. This method calculated x_c=0,79, and this value was therefore utilized in both methods for comparison. The temperature dependence in Flory-Huggins method increase the deviation between these two methods when x_c=0,79 was utilized. Concentration of monomer in the polymer particles was temperature dependent, and this could have been included in the simple method. This method was derived to be simple and including temperature dependence would destroy the simplicity of the method. The simple method was probably most suited to be fitted to measured values, as this method consisted of only one parameter. This was the critical conversion, and if measured values were available for $[M]_p$ the critical conversion could have been tuned to fit the measured values. The Flory-Huggins method depends on four parameters, these are utilized to calculate the interaction parameter. These are more difficult to tune to achieve acceptable match between predicted and measured values. Flory-Huggins predicts more variables, but for temperature control it is enough to predict $[M]_p$. Measurements are expensive or impossible to perform in polymerization reactors, and a method to calculate such an important variable as $[M]_p$, that does not require different parameters is therefore favorable. The simple solution should be verified, and utilized in modeling if it gives acceptable results.

The predicted average number of radicals per particle was in the range given from literature. The new method that calculates moles of radicals in the polymer particles gave reasonable predictions, and this was validated by comparing this with *N(j)* solved as states. The new method seems to be a clever and readily method to calculate moles of radicals in the polymer particles, and the equations are logical and readily to understand. This method also reduces number of states in the model and this is preferred when the model is utilized for control purpose. Actually, when *N(j)* was solved as states, which initial values utilized were important. If *j* was a large number, i.e. moles of particles with 5 radicals, N(5) was a significant low number (10^{-20} moles) and this made some problem in the numerical integration. The tolerance in MATLAB had to be low for the ODE solver utilized, and this increased calculation time. The problem could also be how this was programmed in MATLAB, but it is not irregular that this occurs in such models. The new method is recommended to achieve a simple model that predicts reasonable values for the radical distribution. The zero-one system could not be utilized in this case, because of problems in the MATLAB file.

The predicted and calculated value for moles of particles were quite close in value. The coverage degree of the surfactant was important in this calculation, and a value for the coverage degree was not exact given. This was given as an interval (cannot be given as this is confidential), but the coverage degree of the surfactant was altered so the predicted value got correct. The utilized value of the coverage degree was in the given interval. Surfactant was post-dosed in this process, but this only contributes to make the reaction mixture more stable. N_p was a state and the dynamic was rapid, so steady state was reached after 60-80 seconds. This should therefore be solved as steady state, but since the method for calculating moles of particles made this difficult in the programming file, this was not performed. If N_p had been solved as a steady state, the stiffness in the system would most likely be reduced.

The validation of the model performed with another batch with different recipe and temperature, gave satisfying results. The small alteration that was done in desorption rate constant made the fit better. The given conversion in this batch was different from the first batch utilized, and as desorption rate was estimated as a function of this conversion, k_{de} should be altered when a new batch is utilized. From the results of this case, the sub-models should be possible to use for NMPC. The sub-models were solved as an ODE system, and DAE systems were not necessary to consider. The prediction of the variables seemed to be acceptable and a reasonable match between measured and predicted values were possible to achieve as parameters were estimated by off-line estimation. The calculation time of the model was short but an iteration solved with *fsolve* increased the calculation time significantly. The simple method can be utilized instead of the equation that require iteration, or another method for iteration than using *fsolve* in MATLAB should be utilized. Stiffness in the model was reduced when the simple methods were utilized. If N_p had been solved as a steady state and the zero-one-system had been utilized the model would become less stiff. As control has only been a perspective in this thesis and not a main topic, NMPC has not been tested for the model.

Chapter 8

Conclusion and further work

8.1 Conclusion

The work has involved an extensive search for, and review of emulsion polymerization literature, in order to learn the process and the challenges that were faced during modeling and control of these processes. A toolbox for generation of nonlinear control models for semi-batch emulsion polymerization reactors was made. Some requirements were given for these sub-models. They should be usable for a variety of industrial scale emulsion polymerizations, be easily expandable, suited for NMPC and be utilized for modeling of different products. Mathematical dynamical models were modeled and implemented in MATLAB. To make a dynamic model and utilize this for control in an emulsion polymerization process, basic knowledge about the process were required, and this theory was barely touched in the start of this work.

8.1.1 Modeling and library of sub-models and functions

The modeling has been challenging and some parts of the process have been more difficult to model than others. To model such a complex process, assumptions had to be utilized. In emulsion polymerization a large amount of various reactions occurs, and only some of them were considered in the modeling. Some variables were modeled with different methods to see if it was possible to decrease model stiffness, make a simpler model and to decrease numbers of unknown parameters. The polymerization rate depended on both concentration of monomer in the polymer particle, moles of radicals in the polymer particles and propagation rate constant. All these variables had to be modeled such that they gave reasonable predictions for the polymerization rate. Some of these variables were modeled from different methods, and a library with all the different sub-models was made. All models and sub-models derived were programmed in MATLAB as functions, where a stiff ODE solver (ODE15s) was utilized, as the complete model of the system was stiff for some sub-models. The model could be solved as an ODE system, with only intermediate calculation, independent of methods utilized to model the different variables. This made the model more suitable for control purpose.

Three methods were found for calculation of monomer concentration in polymer particle ($[M]_p$) for both Interval II and III, as Interval I was implemented in Interval II. All methods could be utilized, dependent on parameters available. As the task was to perform some model simplification, a simple method for calculation of $[M]_p$ was found. The simple method did only require one parameter to calculate $[M]_p$ and this was the critical conversion. Critical conversion could be found by measurements or by calculation. The more comprehensive method utilized to calculate $[M]_p$ consisted of solving Flory-Huggins equation to calculate the polymer volume fraction in the polymer-rich phase (φ_p). This method introduced some parameters to calculate Flory-Huggins interaction parameters, that influenced the calculated value of φ_p and further influenced the value of $[M]_p$. This method gave more information than the simple method, as amount of monomer in all four phases was calculated. For control purpose it could be enough to have predictions about $[M]_p$, and both methods calculate the pressure. The third method that could calculate $[M]_p$ and amount of monomer in gas and water phase, was the partition coefficient method. This method required that the partition coefficients were known.

Three different sub-models that calculate the radical distribution were implemented in MATLAB. Independent of sub-model utilized, the balances on the number of particles *N(j)*, containing *j* radicals, had to be found. This balance gave a set of differential equations, and number of equations in this set depended on how large *j* was decided to be. *N(j)* could be solved as states in the model, and initial values had to be found to do this. Another solution was derived in this work, where all balances for moles of particles *N(j)* were solved as steady state. This method introduced a new state in the model; total moles of radicals in the reactor. This method was readily to implement in MATLAB, and it gave a new expression for the polymerization rate. The last sub-model derived to calculate the radical distribution was called the zero-one-system. This method gave a less stiff system, but it could only be utilized to model processes where the average number of radicals per polymer particle was less than 0,5. Other variables were also modeled to achieve a complete model, i.e. moles of particles in the reactor and moment balances. Mole and energy balances were also included.

Modeling performed was programmed in MATLAB, and most of the intermediate calculation and sub-models were programmed as functions. These were readily to utilize and it was possible to expand the library by including new functions. Different product grades could be modeled by using the library, as alteration in recipe and reactor configuration was readily to perform. CTA, inhibitor and other chemicals could be utilized to make various products, and these chemicals had been included in the sub-models. It was not time-consuming to alter the energy and mole balances to account for a CSTR reactor, as they were modeled for a semi-batch reactor. A separate *emulsion_parameter* file was made so both amount and physical values for all species utilized can be altered, and also information about the frequency factor and activation energy for the different reactions. The library consists of all m-files made, and it is a good basis for further development.

8.1.2 Library tested on a case and estimation of parameters

Sub-models given in the library were tested on a case, to verify if all methods derived for the different variables gave reasonable predictions. Some measured values were given from Ineos, and these were for a semi-batch emulsion polymerization of poly-vinyl chloride process. As polymerization is extremely exothermic, a cooling jacket was utilized to cool the reactor mixture where among others inlet cooling jacket temperature was controlled. Some sub-models introduced parameters that were unknown and these had to be estimated. This was performed with an off-line estimation with available measured values. The energy balance for the reactor temperature could only be utilized if a controller was implemented in the model. This was tested, but because of time delay and difficulties in the tuning, the model could not predict correct temperature. It was therefore decided to utilize measured inlet cooling temperature, cooling water flow rate and reactor temperature directly into the model.

The estimation of the parameters was divided into two problems. The heat transfer coefficient (U) was estimated by *lsqcurvefit*, which is a part of the Optimization toolbox in Matlab. To estimate U the complete model was changed to not include the kinetic parts and outlet cooling temperature was the only state. Three solutions were tested and all gave acceptable results, so a quadratic polynomial was utilized to express U as a function of conversion combined with three parameters, found by *lsqcurvefit*. Several kinetic rate constants were also unknown, and these were desorption and absorption rate constants in addition to the transfer rate constants. Another parameter that gave some problems was the propagation rate constants. Different literature gave completely different values for the activation energy, frequency factor and reference rate constant for propagation. Literature was utilized as a basis, and an Arrhenius equation was found for the propagation rate where the parameters utilized was in the range of those given in literature. Absorption rate constant was set constant. The desorption rate actually alters with temperature and particle size, but it was not possible to make desorption as a function of these criterias. A readily solution had to be found, and desorption rate was given as a function of conversion. Kinetic parameters estimated were found by fitting the measured and predicted conversion. The measured conversion was actually calculated from the energy balance, and the accuracy of this conversion was unknown. Estimation was not readily to perform, because the model was too comprehensive compared with available process data. The transfer rate constants were therefore not possible to estimate, and the moment balances were not tested for this case.

The model was simulated for the whole batch time with parameters found from estimation, and different variables were predicted by the model. Moles of particles were close to the value found by calculations, when the coverage degree of the surfactant was in the range of the values given and the desorption rate was low in the start. The dynamic of moles of particles was rapid, and after 60-80 seconds a steady state solution was found. Moles of particles were therefore not necessary to solve as a state, and a steady state solution could have been found. To calculate $[M]_p$ both the simple method and the more comprehensive Flory-Huggins method were utilized. If the parameters for the Flory-Huggins method had been estimated for this process, this method would probably give more reasonable predictions. This method predicted the critical conversion to be approximately 0.79, but it was found from measured values to be 0,77 for the batch. The simple method was probably most suited to be fitted to measured values and seemed to predict acceptable values for the concentration of monomer in the polymer particles. This could not be confirmed without measured values of $[M]_p$. Predicted pressure had an acceptable fit in Interval I and II, but in Interval III there was a rapid pressure drop in the model. This occurred independent of which method utilized to calculate the pressure. This did not occur in the real reactor, as the temperature increase in the end was so large that the total pressure would not drop. There can be different reasons for this deviation, and some theories are lack of dynamic in the model. The model predicts a rapid decrease of monomer in the gas phase in interval III, but this was probably too rapid compared with the real process. Some uncertainties in the measure conversion given were also found, and the critical conversion utilized in the model can be incorrect. Parameters were estimated to match predicted and measured conversion, and this can introduce more uncertainties in the predictions from the model. The deviation in the pressure predictions in Interval III should be study further, as pressure control is normal to utilize in emulsion polymerization processes. Moles of particles with zero, one, two, etc. radicals were readily to find by solving *N(j)* as a state, but the model was a little sensitive for initial values utilized. This method and the new method derived, predicted the same values through the batch and the new method could therefore be recommended to utilize. The zero-one-system could not be tested on the case, as some problem in the MATLAB file occurred.

The model was validated by testing another batch with different recipe and temperature profile. All parameters found were kept as the first batch, but desorption rate was barely changed. The simple method for calculation of monomer concentration in the polymer particle and the new method for calculation of the radical distribution were used. This gave an acceptable match between predicted and measured conversion, and the rest of the model predictions seemed reasonable.

The sub-models derived in this work fulfill some requirements, which should be achieved if the sub-models would be used for non-linear model predictive control. The model could be solved as an ODE system and the calculation time was rapid independent of sub-model used. By deriving a new method that calculated moles of radicals in the polymer particles, number of states in the model was reduced. Model simplification reduced stiffness in the system, and the simple method used for calculation of $[M]_p$ seemed to predict reasonable values and introduced only one unknown parameter (x_c) in the model.

8.2 Further work

With more time available, this work could have been extended considerable. The emulsion polymerization process involved many challenges and complications that made it difficult to assess the process completely and take everything into account. The thesis work has been carried out without any prior experience with polymerization processes, thus consisting of rather simplified models. Further studies of emulsion polymerization and industry experience would undoubtedly result in a more detailed model. A more suitable method for parameter estimation could be found, and with available data this should be tested on the model. Estimation with trial-and-error was time-consuming. The model should be tested with more available process data, and validate the different methods derived in this work based on real measured values.

Modeling of moles of particles should be studied further, and the solution already given should be solved as steady state. This would reduce stiffness in the model even more. Other efforts should also be studied to reduce the stiffness in the system accordingly. The library should also be expanded, so it consists of other reactor cooling configurations. A reflux condenser can be modeled. The pressure should be studied further, as there was a deviation in Interval III, so other methods used to calculate pressure should be derived. The simple method for calculation of monomer concentration in the polymer particles can be extended to account for the concentration of monomer in the other phases. This can probably be done without utilizing

Flory-Huggins equation. Modeling of the particle size distribution should also be performed, where population balances have to be found. A model that predicts PSD can be preferred in some situations for control purpose.

All models are built to be suited for NMPC, but how suited the sub-models are for NMPC can only be found if NMPC is implemented. This should be done, and then results on how usable the model is will be revealed. The first idea behind this thesis was to model all sub-models in Modellica, but since this program was unknown for the author is was not performed. Further work would be to look into the potential to move all sub-models made in MATLAB into other programs that can readily be linked with other programs that i.e. implements NMPC.

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Appendix A

Derivation of equations

In this appendix derivation of some of the equations will be given. This is done to give the reader a better understanding of the equation used.

A.1 Zero-One system

As the average number of radicals per particle is low for PVC («0,5) a quasi-steady state calculations of the radical distribution in particles, assuming a zero-one system was tried. Assumptions made in this solution are listed below:

- Number of particle with two or more radicals can be neglected, as this amount is small compared to amount of particle with zero and one radicals.
- Immediately after radicals number two enters a particle the particle chain terminate instantaneous

Three simple balance equations for moles of particles with zero, one and two radicals can be given in Equation A.1.1, as for this zero-one assumption the other balance equations for particles with higher number of radicals are neglected. It should also be mentioned that it is not difficult to account for moles of particles with two radicals. This is a small number compared to N_1 in i.e. the PVC process.

$$\begin{aligned}\frac{dN_0}{dt} &= -k_a N_{rw} N_A N_0 + \frac{2k_t}{v_p N_A} N_2 + k_{de} N_1 \\ \frac{dN_1}{dt} &= k_a N_{rw} N_A (N_0 - N_1) - k_{de} N_1 + \delta(1) r_p \\ \frac{dN_2}{dt} &= k_a N_{rw} N_A N_1 - \frac{2k_t}{v_p N_A} N_2\end{aligned} \tag{A.1.1}$$

The equations are solved as steady state, and the last one is solved for N_2 and this is put into the two other equation so that N_2 disappear. Two relations are used to find a readily solution, and these two are given in Equation A.1.2.

$$\begin{aligned}N_{particles} &= N_0 + N_1 + N_2 \\ N_R &= N_{rw} + N_1 + 2N_2\end{aligned} \tag{A.1.2}$$

The steady state solution of the balances are used to get one equation for the population balances (can chose which one to use, they will off course give the same answer). The equation that is left are given in Equation A.1.3. The radical balance is given in Equation A.1.4.

$$k_a N_{rw} N_A N_0 - k_a N_{rw} N_A N_1 - k_{de} N_1 = 0 \tag{A.1.3}$$

$$\frac{dN_R}{dt} = 2fk_I N_{Ini} - \frac{2k_t}{v_p N_A} 2N_2 = 2fk_I N_{Ini} - 2k_a N_{rw} N_A N_1 \tag{A.1.4}$$

The steady state solution of the radical balances is utilized and this gives two equations with two unknowns given in Equation A.1.5. These are used to solve for N_1, and this is given in Equation A.1.6.

$$\begin{aligned} 0 &= 2fk_I N_{Ini} - 2k_a N_{rw} N_A N_1 \\ 0 &= k_a N_{rw} N_A (N_p - 2N_1) - k_{de} N_1 \end{aligned} \tag{A.1.5}$$

$$\begin{aligned} &N_{rw} = \frac{fk_I N_{ini}}{k_a N_A N_1} \\ &0 = \frac{fk_I N_{ini}}{N_1} N_p - fk_I N_{Ini} - k_{de} N_1 \\ &\underline{0 = fk_I N_{Ini} N_p - fk_I N_{Ini} N_1 - k_{de} {N_1}^2} \end{aligned} \tag{A.1.6}$$

This given a new expression for the polymerization rate, and this is given in Equation A.1.7.

$$R_p = k_p [M]_p N_1 \tag{A.1.7}$$

A.2 Moment equations

Some of the moment equation will be derived. This is only to show the reader how readily they can be found. When deriving these moment equations, the kinetics utilized was first chosen. The derivation of the zero and first live moments are given. Some rule/equation used is given in Equation A.2.1, A.2.2, A.2.3 and A.2.4. All these are used in the derivation. [13]

$$\mu_0 = \sum_{j=1}^{\infty} [P_j] \tag{A.2.1}$$

$$[P_1] + \sum_{n=2}^{\infty} [P_n] = \mu_0 \tag{A.2.2}$$

$$\frac{d\mu_0}{dt} = \frac{dP_1}{dt} + \sum_{n=2}^{\infty} \frac{dP_n}{dt} \tag{A.2.3}$$

$$\sum_{n=2}^{\infty} [P_{n-1}] = \sum_{n=1}^{\infty} [P_n] = \mu_0 \tag{A.2.4}$$

Equations for P_1 and P_n are given in Equation A.2.5 and A.2.6, and these are put into Equation A.2.3.

$$\begin{aligned}
\tfrac{dP_1}{dt} &= 2fk_I[I] - k_p[P_i][M] - k_{tc}\mu_0[P_1] - k_{td}\mu_0[P_1] + k_{tr}^{mon}[M]\mu_0 + k_{tr}^{CTA}[CTA]\mu_0 \\
&-\{k_{tr}^{mon}[M][P_1] + k_{tr}^{CTA}[CTA][P_1]\} \\
&-k_{tr}^{pol}[P_1]\sum_{j=1}^{\infty} j[D_j] + k_{tr}^{pol}[D_1]\mu_0
\end{aligned} \tag{A.2.5}$$

$$\begin{aligned}
\tfrac{dP_n}{dt} &= k_p[M]([P_{n-1}] - [P_n]) - \{k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA] + (k_{td} + k_{tc})\sum_{j=1}^{\infty}[P_j]\}[P_n] \\
&+k_{tr}^{pol} n[D_n]\sum_{j=1}^{\infty}[P_j] - k_{tr}^{pol}[P_n]\sum_{j=1}^{\infty} j[D_j]
\end{aligned} \tag{A.2.6}$$

The derivation and end equation for the zero and first moment of live polymer is given in A.2.7 and A.2.8.

$$\begin{aligned}
\tfrac{d[\mu_0]}{dt} &= 2fk_I[I] - k_p[P_1][M] - [\mu_0][P_1](k_{td} + k_{tc}) + (k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA])[\mu_0] \\
&-(k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA])[P_1] - k_{tr}^{pol}[P_1]\sum_{j=1}^{\infty} j[D_j] + k_{tr}^{pol}[D_1][\mu_0] + \{\sum_{n=2}^{\infty} k_p[M]([P_{n-1}] - [P_n]) \\
&-\{k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA] + (k_{td} + k_{tc})\sum_{j=1}^{\infty}[P_j]\}[P_n] + k_{tr}^{pol} n[D_n]\sum_{j=1}^{\infty}[P_j] - k_{tr}^{pol}[P_n]\sum_{j=1}^{\infty} j[D_j]\} \\
\tfrac{d[\mu_0]}{dt} &= 2fk_I[I] - k_p[P_1][M] + \sum_{n=2}^{\infty} k_p[M]([P_{n-1}] - [P_n]) - \{[\mu_0](k_{td} + k_{tc})([P_1] + \sum_{n=2}^{\infty}[P_n])\} \\
&-\{(k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA])([P_1] + \sum_{n=2}^{\infty}[P_n]\} + (k_{tr}^{mon}[M] + k_{tr}^{CTA}[CTA][\mu_0]) \\
&-k_{tr}^{pol}[P_1]\sum_{j=1}^{\infty} j[D_j] + k_{tr}^{pol}[D_1][\mu_0] + \sum_{n=2}^{\infty}\{k_{tr}^{pol} n[D_n][\mu_0] - k_{tr}^{pol}[P_n]\sum_{j=1}^{\infty} j[D_j]\} \\
\tfrac{d[\mu_0]}{dt} &= 2fk_I[I] - \{k_p[M]([P_1] + \sum_{n=2}^{\infty}[P_n])\} + k_p[M]\sum_{n=2}^{\infty}[P_{n-1}] - [\mu_0]^2(k_{td} + k_{tc}) \\
&+k_{tr}^{pol}[\mu_0]([D_1] + \sum_{n=2}^{\infty} n[D_n]) - k_{tr}^{pol}[\nu_0]([P_1] + \sum_{n=2}^{\infty}[P_n]) \\
&\underline{\underline{\tfrac{d[\mu_0]}{dt} = 2fk_I[I] - [\mu_0]^2(k_{td} + k_{tc})}}
\end{aligned}$$

(A.2.7)

$$\frac{d[\mu_1]}{dt} = P_1 + \sum_{n=2}^{\infty} n\frac{dP_n}{dt}$$
$$\frac{d[\mu_1]}{dt} = 2fk_I[I] - k_p[P_1][M] - [\mu_0][P_1](k_{td}+k_{tc}) + (k_{tr}^{mon}[M]+k_{tr}^{CTA}[CTA])[\mu_0]$$
$$-(k_{tr}^{mon}[M]+k_{tr}^{CTA}[CTA])[P_1] - k_{tr}^{pol}[P_1]\sum_{j=1}^{\infty} j[D_j] + k_{tr}^{pol}[D_1][\mu_0] + \{\sum_{n=2}^{\infty} n(k_p[M]([P_{n-1}]-[P_n])$$
$$-\{k_{tr}^{mon}[M]+k_{tr}^{CTA}[CTA]+(k_{td}+k_{tc})\underbrace{\sum_{j=1}^{\infty}[P_j]}_{\mu_0}\}[P_n] + k_{tr}^{pol}n[D_n]\sum_{j=1}^{\infty}[P_j] - k_{tr}^{pol}[P_n]\sum_{j=1}^{\infty} j[D_j])\}$$
$$\frac{d[\mu_1]}{dt} = 2fk_I[I] - k_p[M]\underbrace{(P_1+\sum_{n=2}^{\infty} nP_n)}_{\mu_1} + k_p[M]\underbrace{(\sum_{n=2}^{\infty} nP_{n-1})}_{\mu_0+\mu_1} - [\mu_0](k_{td}+k_{tc})\underbrace{([P_1]+\sum_{n=2}^{\infty} nP_n)}_{\mu_1}$$
$$+(k_{tr}^{mon}[M]+k_{tr}^{CTA}[CTA])[\mu_0] - (k_{tr}^{mon}[M]+k_{tr}^{CTA}[CTA])\underbrace{([P_1]+\sum_{n=2}^{\infty} nP_n)}_{\mu_1}$$
$$-k_{tr}^{pol}\underbrace{([P_1]+\sum_{n=2}^{\infty} nP_n)}_{\mu_1}(\sum_{j=1}^{\infty} j[D_j] + \sum_{n=2}^{\infty} n\sum_{j=1}^{\infty} j[D_j])) + k_{tr}^{pol}\underbrace{([D_1]+\sum_{n=2}^{\infty} n^2D_n)}_{\nu_2}([\mu_0] + \sum_{n=2}^{\infty} n\sum_{j=1}^{\infty}[P_j])$$
$$\frac{d[\mu_1]}{dt} = 2fk_I[I] - k_p[M][\mu_0] - [\mu_0](k_{td}+k_{tc})[\mu_1] + (k_{tr}^{mon}[M]+k_{tr}^{CTA}[CTA])([\mu_0]-[\mu_1])$$
$$+k_{tr}^{pol}([\mu_0][\nu_2]-[\mu_1][\nu_1]) \tag{A.2.8}$$

A.3 Simple method: Total polymer particle volume, monomer concentration in the polymer particles and pressure

This method calculate the total volume of particles and concentration of monomer in the polymer particles. In this method, monomer in gas and water phase is neglected. Pressure can also be calculated. Both Interval II and III will be considered separately. When the critical conversion is reached (x_c) Interval II is finished and Interval III starts.

A.3.1 Interval II

The total volume of particles in given in Equation A.3.1.

$$V_p = V_{p,solid} + V_{m,particle} \tag{A.3.1}$$

An expression for these two volumes is given in Equation A.3.2 and A.3.3.

$$V_{p,solid} = \frac{MW_m X\widetilde{N}_m}{\rho_p} \tag{A.3.2}$$

$$V_{m,particle} = \frac{MW_w \zeta X\widetilde{N}_m}{\rho_m} \tag{A.3.3}$$

Where $N_{reacted,monomer} = X\widetilde{N}_m$ and $N_{m,p} = \zeta N_{reacted,monomer} = \zeta X\widetilde{N}_m$. In these equations ζ is the solubility parameter of monomer in polymer.

This gives the total volume in Equation A.3.4, and a expression for the solubility parameter should be found.

$$V_p = MW_m X\widetilde{N}_m(\frac{1}{\rho_p} + \frac{\zeta}{\rho_m}) \tag{A.3.4}$$

The monomer concentration in the polymer particles can be calculated by using Equation A.3.5.

$$[M]_p = \frac{N_{m,p}}{V_p} = \frac{\zeta X\widetilde{N}_m}{MW_m X\widetilde{N}_m(\frac{1}{\rho_p} + \frac{\zeta}{\rho_m})} = \frac{\zeta}{MW_m(\frac{1}{\rho_p} + \frac{\zeta}{\rho_m})} = \frac{\zeta\rho_m\rho_p}{MW_m(\rho_m + \zeta\rho_p)} \tag{A.3.5}$$

Concentration is independent of amount and conversion of monomer. This equation is only valid for saturated polymer, and this is in Interval I and II. In the end of Interval II Equation A.3.6 can be used.

$$\widetilde{N}_m = x_c\widetilde{N}_m + \zeta x_c\widetilde{N}_m \rightarrow 1 = x_c + \zeta x_c \tag{A.3.6}$$

An expression for the solubility is used, and this is given in Equation A.3.7) and this is put back into the equation already given for total volume and concentration of monomer in the polymer particles.

$$\zeta = \frac{1 - x_c}{x_c} \tag{A.3.7}$$

The final expressions for concentration and volume are given in Equation A.3.8 and A.3.9.

$$[M]_P = \frac{\frac{1-x_c}{x_c}\rho_m\rho_p}{MW_m(\rho_m + \frac{1-x_c}{x_c}\rho_p)} = \frac{(1 - x_c)\rho_m\rho_p}{MW_m(\rho_p - x_c\rho_c + x_c\rho_m)} = \underline{\underline{\frac{(1 - x_c)\rho_m}{(1 - x_c + x_c\rho_m/\rho_p)MW_M}}} \tag{A.3.8}$$

$$V_p = MW_m X\widetilde{N}_m(\frac{1}{\rho_p} + \frac{1 - x_c}{x_c\rho_m}) \tag{A.3.9}$$

A.3.2 Interval III

In interval III the polymer is not saturated and a new equation is used to find moles of monomer in the polymer particle, this is given in Equation A.3.10. Equations given in this section is only valid when X > x_c.

$$N_{m,p} = \widetilde{N}_m - X\widetilde{N}_m = \widetilde{N}_m(1 - X) \tag{A.3.10}$$

Volume of monomer in particle is given in Equation A.3.11.

$$V_{m,particle} = \frac{MW_w\widetilde{N}_m(1-X)}{\rho_m} \tag{A.3.11}$$

The final equations for total volume of particles and concentration of monomer in particle is given in Equation A.3.12 and A.3.13.

$$V_p = \frac{MW_w\widetilde{N}_m(1-X)}{\rho_m} + \frac{MW_w\widetilde{N}_m X}{\rho_p} = MW_w\widetilde{N}_m(\frac{(1-X)}{\rho_m} + \frac{X}{\rho_p}) \tag{A.3.12}$$

$$[M]_p = \frac{N_{m,p}}{V_p} = \frac{\widetilde{N}_m(1-X)}{MW_w\widetilde{N}_m(\frac{(1-X)}{\rho_m} + \frac{X}{\rho_p})} = \frac{(1-X)\rho_m}{(1-X+X\rho_m/\rho_p)MW_M} \tag{A.3.13}$$

The pressure can readily be calculated from this simple method. Moles of monomer in the polymer particles is given for Interval II in Equation A.3.14 and for Interval III in Equation A.3.15. For Interval III it is assumed full solubility.

$$N_{m,p} = \widetilde{N}_m - X\widetilde{N}_m = \widetilde{N}_m(1-X) \tag{A.3.14}$$

$$N_{m,p} = \widetilde{N}_m X\zeta = N_{m,p,\max} \tag{A.3.15}$$

Solubility is found from Equation A.3.7, and an expression for the the monomer activity is found, and this is shown in Equation A.3.16.

$$\alpha_m = \frac{N_{m,p}}{N_{m,p,\max}} \tag{A.3.16}$$

In Interval I and II, $\alpha_m = 1$, but for Interval III α_m is found from Equation A.3.17.

$$\alpha_m = \frac{\widetilde{N}_m(1-X)}{\widetilde{N}_m\zeta} = \frac{(1-X)}{X}\frac{1}{\zeta} = \frac{1-X}{1-x_c}\frac{x_c}{X} \tag{A.3.17}$$

Pressure for Interval I and II is equal to the saturation pressure of water and monomer, but the pressure in Interval III is found by using Equation A.3.18.

$$P = \alpha_m P_{sat} \tag{A.3.18}$$

A.4 Material balances

To perform a mole balance on any system the boundaries of the system have to be specified. The volume enclosed by these boundaries is referred to as the system volume. A mole balance can be given simple as; In-Out+Generation=Accumulation. This is given in Equation A.4.1. From this it is readily to understand how to find mole balances for a system. [43]

$$F_{j,in} - F_{j,out} + G_j = \frac{dN_j}{dt} \tag{A.4.1}$$

A.5 Energy balances

For an open system some of the energy exchange is because of the flow of mass across the system boundaries. Rate of accumulation of energy within the system is given in Equation A.5.1. It is assumed that the system volume is well mixed. [43]

$$\frac{d\widehat{E}_{sys}}{dt} = Q' - W_s{}' + \sum_{i=1}^{n} (F_i E_i)_{in} - \sum_{i=1}^{n} (F_i E_i)_{out} \tag{A.5.1}$$

The work term (W) is evaluated, and this is often separated into flow work and other work. The shaft work is often referred to with W_s, and this could be produced from i.e. a stirrer in a CSTR or a turbine in a PFR. Flow work is work that is necessary to transport the mass into and out of the system, and this is given in Equation A.5.2. The units can be mentioned, and F_i is in *mole/s*, pressure P in *Pa* and V_i is in *m*^{3}*/mole*. This given the work term in *Watts*.

$$W' = -\sum_{i=1}^{n} (F_i P V_i)_{in} + \sum_{i=1}^{n} (F_i P V_i)_{out} + W_s{}' \tag{A.5.2}$$

Next the flow work term is combined with those terms in the energy balances that represent the energy exchange by mass flow across the system boundaries (Equation A.5.3). The energy E_i is the sum of different energy forms like, internal energy, kinetic energy, potential energy and others. In most chemical reactor situations, the kinetic, potential and "others" energy terms are negligible in comparison with the enthalpy, heat transfer and work terms (E_i=U_i).

$$\frac{d\widehat{E}_{sys}}{dt} = Q' - W_s{}' + \sum_{i=1}^{n} (F_i(E_i + PV_i))_{in} - \sum_{i=1}^{n} (F_i(E_i + PV_i))_{out} \tag{A.5.3}$$

Enthalpy is defined in terms of the internal energy U_i and the product PV_i ($H_i = U_i + PV_i$). The new energy balance is given in Equation A.5.4.

$$\frac{d\widehat{E}_{sys}}{dt} = Q' + W_s{}' + \sum_{i=1}^{n} (F_i H_i)_{in} - \sum_{i=1}^{n} (F_i H_i)_{out} \tag{A.5.4}$$

Next $\widehat{E}_{sys}$ is evaluated, and this is done in Equation A.5.5.

$$\widehat{E}_{sys} = \sum_{i=1}^{n} N_i E_i = \sum_{i=1}^{n} N_i U_i = (\sum_{i=1}^{n} N_i (H_i - PV_i))_{sys} = \sum_{i=1}^{n} N_i H_i - P \underbrace{\sum_{i=1}^{n} N_i V_i}_{V} \tag{A.5.5}$$

For further equation a simpler form for writing the sum will be used: $\sum = \sum\limits_{i=1}^{n}$. No spatial variations in the system volume are assumed, and time variations in product of the total pressure and volume are neglected, the energy balance take a new form given in Equation A.5.6. A large number of chemical reactions in industry do not involve phase change, and the energy balance applies to single-phase chemical reactions. Under these conditions the enthalpy of species i at temperature T is related to the enthalpy of formation at the reference temperature T_{ref} by enthalpy given in Equation A.5.7.

$$Q' + W_s{}' + \sum (F_i H_i)_{in} - \sum (F_i H_i)_{out} = (\sum N_i \frac{dH_i}{dt} + \sum H_i \frac{dN_i}{dt})_{sys} \tag{A.5.6}$$

$$H_i = H(T_{ref}) + \int_{T_{ref}}^{T} C_{pi} dT \tag{A.5.7}$$

Differentiating Equation A.5.7 with respect to time, we obtain $\frac{dH_i}{dt} = C_{P_i}\frac{dT}{dt}$, this is used in the energy balance and a new form is obtained with temperature (Equation A.5.8).

$$Q' + W_s{}' + \sum (F_i H_i)_{in} - \sum (F_i H_i)_{out} = \sum C_{pi} N_i \frac{dT}{dt} + \sum H_i \frac{dN_i}{dt} \tag{A.5.8}$$

Next step is to use the mole balance and put this into the energy balance. This mole balance will be different dependent on if it is a semi-batch, batch or CSTR reactor. In this case a mole balance for a CSTR is used, as the energy balance have already been given for a CSTR case as it has considered both inlet and outlet streams. These are of course not included in an energy balance for a batch reactor, so these terms can be deleted for a batch reactor. The mole balance is given in Equation A.5.9, and this included in the energy balance give a new form of the energy balance given in Equation A.5.10.

$$\frac{dN_i}{dt} = -v_i r_A V + F_{i,in} - F_{i,out} \tag{A.5.9}$$

$$\frac{dT}{dt} = \frac{Q' + W_s{}' - \sum F_{i,in}(H_{i,out} - H_{i,in}) + (-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{p_i}} \tag{A.5.10}$$

For a batch reactor where there are no inlet and outlet streams, the energy balance is given in Equation A.5.11. All equation given are for general cases.

$$\frac{dT}{dt} = \frac{Q' + W_s{}' + (-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{p_i}} \tag{A.5.11}$$

A.6 Balance for total number of radicals

To find the balance for total number of radicals population balances were derived in combination with some equations. The derivation of equation for total number of radicals will also show if the population balances are correct. This derivation will be given here.

First given is all population balances, and this have already been given in Section 5.2.5. Total number of particles and radicals are found by using Equation A.6.1 and A.6.2. To show how the total radicals balance is found j_{max}=4 is used. This can actually be any number. It should be mentioned that the inhibitor term is not considered, but this is readily to include.

$$N_{particles} = N_0 + N_1 + N_2 + N_3 + N_4 \tag{A.6.1}$$

$$\frac{dN_R}{dt} = \frac{dN_{Rw}}{dt} + \frac{dN_1}{dt} + 2\frac{dN_2}{dt} + 3\frac{dN_3}{dt} + 4\frac{dN_4}{dt} \tag{A.6.2}$$

The population balances and the balance for moles of radicals in the water phase are put into Equation A.6.2.

$$\begin{aligned}
&\tfrac{dN_R}{dt} = 2fk_I N_{ini} - k_a N_{rw} N_A (N_0 + N_1 + N_2 + N_3 + N_4) + k_{de}(N_R - N_{Rw}) \\
&+k_a N_{rw} N_A (N(0) - N(1)) + \tfrac{6k_t}{v_p N_A} N(3) - k_{de}(N(1) - 2N(2)) \\
&+2[k_a N_{rw} N_A (N(1) - N(2)) + \tfrac{k_t}{v_p N_A}(12N(4) - 2N(2)) - k_{de}(2N(2) - 3N(3))] \\
&+3[k_a N_{rw} N_A (N(2) - N(3) - N(4)) - \tfrac{k_t}{v_p N_A}(6N(3)) - k_{de}(3N(3) - 4N(4))] \\
&+4[k_a N_{rw} N_A (N(3) + N(4)) - \tfrac{k_t}{v_p N_A}(12N(4)) - k_{de}(4N(4))]
\end{aligned} \tag{A.6.3}$$

Most of the terms in Equation A.6.3 will be neglected, and the ones left are given in Equation A.6.4.

$$\begin{aligned}
&\tfrac{dN_R}{dt} = 2fk_I N_{ini} + \tfrac{6k_t}{v_p N_A} N(3) + \tfrac{2k_t}{v_p N_A}(12N(4) - 2N(2)) - \tfrac{3k_t}{v_p N_A}(6N(3)) - \tfrac{4k_t}{v_p N_A}(12N(4)) \\
&= 2fk_I N_{ini} - \tfrac{k_t}{v_p N_A}(4N(2) + 12N(3) + 24N(4))
\end{aligned} \tag{A.6.4}$$

This given the equation for total moles of radicals, and this is seen in Equation A.6.5.

$$\frac{dN_R}{dt} = 2fk_I N_{ini} - \frac{2k_t}{v_p N_A} \sum_{j=0}^{\infty} (j+2)(j+1) N_{j+2} \tag{A.6.5}$$

A.7 Calculation of Flory-Huggins interaction parameter

Flory-Huggins interaction parameter, χ, can be given as the sum of an enthalpy, entropic and interfacial contribution (See Equation A.7.1). [7]

$$\chi = \chi_H + \chi_S + \chi_I \tag{A.7.1}$$

The enthalpy contribution to the interaction parameter can be calculated from the solubility parameters (δ_1 and δ_2), and this is given in Equation A.7.2.

$$\chi_H = \frac{V_1((\delta_1 - \delta_2)^2 + 2\delta_1 \delta_2 I_{12})}{RT_R} \tag{A.7.2}$$

I equation A.7.2 V_1 is the molar volume of the solvent in the polymer solvent mixture. Interaction parameter will from this depend on both the polymer volume fraction and the polymerization temperature. These two factors are therefore included in the calculation of the interaction parameter, and this is performed through the introduction of an appropriate expression for the calculation of I_{12} (See Equation A.7.3).

$$I_{12} = a + b\varphi_p^2 + c\varphi_p + d/T_R \tag{A.7.3}$$

In this equation a, b, c and d are adjustable parameters which should be fitted by using measured process data [7]. The entropic contribution of the interaction parameter can be found in literature or with experiment. The contribution of the interfacial contribution is often neglected. The solubility parameters should be calculated, and this is given as the square root of the ratio of the cohesive energy over the solvent molar volume (See Equation A.7.4). [7]

$$\delta_1 = \sqrt{\frac{E_{coh1}}{V_1}} \tag{A.7.4}$$

A.8 Calculation of virial coefficients

Viral coefficients of a pure substance is given as B_i and for a binary mixture it is given as B_{ij}. This viral coefficients are related to the accentric factors ω_i and ω_{ij} . The equations for calculations for the virial coefficients are given in A.8.1 and A.8.2. [7] [31]

$$B_i = \frac{RT_{c,i}}{P_{c,i}}(B_i^0 + \omega_i B_i^1) \tag{A.8.1}$$

$$B_{ij} = \frac{RT_{c,ij}}{P_{c,ij}}(B_{ij}^0 + \omega_{ij} B_{ij}^1) \tag{A.8.2}$$

The values for B^0 and B^1 is found by using the reduced temperature, T_r ($T_r = \frac{T}{T_c}$), and this is given in Equation A.8.3 and A.8.4.

$$B_i^0 = 0.083 - \frac{0.422}{T_{r,i}^{1.6}} \tag{A.8.3}$$

$$B_i^1 = 0.139 - \frac{0.172}{T_{r,i}^{4.2}} \tag{A.8.4}$$

Pseudocritical properties of a pair (i-j) of components are given by Equation A.8.5, A.8.6, A.8.7, A.8.8 and A.8.9.

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \tag{A.8.5}$$

$$T_{c,ij} = (T_{c,i} T_{c,j})^{0.5} \tag{A.8.6}$$

$$P_{c,ij} = \frac{Z_{c,ij} R T_{c,ij}}{V_{c,ij}} \tag{A.8.7}$$

$$Z_{c,ij} = \frac{Z_{c,i} + Z_{c,j}}{2} \tag{A.8.8}$$

$$V_{c,ij} = (\frac{{V_{c,i}}^{1/3} + {V_{c,j}}^{1/3}}{2})^3 \tag{A.8.9}$$

Appendix B

Matlab

B.1 Table with all MATLAB files

The MATLAB scripts and functions that were used in order to produce the results of this project are attached in this section, a list of the file names and descriptions are presented in Table B.1. In the files given, the values of the parameters are not actual, and they should not be associated with the case.

Table B.1: Library; Sub-models as m-files

File name	Description
main_model.m	Run model and plot the results
model.m	Model file, states and intermediate calculations. Other function are called.
emulsion_parameters.m	Process parameters defined
rate_constants.m	Calculate and specify rate constants.
monomer_concentration_particle.m	Calculate monomer in particle, simple methode
monomer_concentration_coeff.m	Calculate monomer concentration in particle using partition coefficients
monomer_concentration_4phase.m	Calculate monomer in particle, using Flory-Huggins eq.
saturation_pressure.m	Calculate saturation pressure
pressure.m	Calculate pressure in Interval III
density_process.m	Calculate density, values for PVC given
virial_coeff.m	Calculate virial coefficients
flory.m	Calculate polymer volume fraction
coeffFlory.m	Calculate interaction parameter
floryIII .m	Calculate activity in Interval III
model_radicals_states.m	N(j) solved as states, with j_{max}=4
radical_matrix .m	Matrices found for calculation of radical distribution; new method
zero_one_system.m	Zero one system, radical distribution
moment_equations.m	Give six moment equation, and PDI.
main_curvefit_U.m	First part curvefit U
main_estimation_curvefit_ode15s.m	Second part curvefit U
estimation_U.m	Third part curvefit U

B.2 MATLAB files

B.2.1 Main model

This file have to be used to run the model. This solves the ODE with using ODE15s. The model function is also called again, and this is done to be able to take out information about the intermediate calculations.

```
%*************************************************************************
% Name     : main_model
% Function : Solve the ODEs, and simulate the whole batch
% Author   : Anette H. Helgesen 2011
%*************************************************************************
load 2oct10
par = emulsion_parameters();
%% Timespan and states
```

```
t_end=31620;
tspan1=[0:10:4840];
tspan2=[4850:10:18700];
tspan3=[18710:10:t_end];
times=[];
States=[];
%% Initial values for the states.
x10=[14.4617 1e-10 139204 1e-10 359 8.8176];
options=odeset('BDF','on','AbsTol',1e-06,'RelTol',1e-06); %,'maxStep',0.0001
format short G
Nm_in=139204;
Tr=data((359:3521),7)+273.15;
Tjin=data((359:3521),5)+273.15;
Xi=data((359:3521),2)/100;

%% ODE solver
%After dosing of emulgator, but not in this interval of the batch time
Emu=0; Ve2=0; m_em2_tot=0; Win=0; cin=0; Tin=0;
tic
[T,x1]= ode15s(@model,tspan1,x10,options,par,Emu,Ve2,m_em2_tot,Win,cin,Tin,Tjin,Tr,Xi);

times=[times;T];
States=[States;x1];
% Start next interval of batch with putting more surfactant into reactor.
x20 = x1(end,:)';
Emu=0.1; Ve2=200; m_em2_tot=50000; Win=0.05; cin=4; Tin=300;
[TT,x2]=ode15s(@model,tspan2,x20,options,par,Emu,Ve2,m_em2_tot,Win,cin,Tin,Tjin,Tr,Xi);
times=[times;TT];
States=[States;x2];

x30 = x2(end,:)';
Emu=0; Ve2=0; m_em2_tot=0; Win=0; cin=0; Tin=0;
[TTT,x3]=ode15s(@model,tspan3,x30,options,par,Emu,Ve2,m_em2_tot,Win,cin,Tin,Tjin,Tr,Xi);
times=[times;TTT];
States=[States;x3];

nstep=length(times);
N_bar=zeros(size(times));
X=zeros(size(times));
N_polymer=zeros(size(times));
Rp=zeros(size(times));
Mp=zeros(size(times));

%Parameters and intermediate calculations in function
for i=1:nstep
    State=States(i,:);
    [F N_bar(i) X(i) N_polymer(i) Rp(i) Mp(i)] = model(times(i),State,par,Emu,Ve2,m_em2_tot,↩
        Win,cin,Tin,Tjin,Tr,Xi);

end
toc
```

B.2.2 Model

This file is a function which build up a complete model for an emulsion polymerization process. This include data given into the model, the states and intermediate calculations.

```
%*************************************************************************
% Name      : model
% Function : A complete model of a emulsion polymerization semi-batch
% Author    : Anette H. Helgesen 2011
%*************************************************************************/
function [F N_bar X N_polymer Rp Mp mat Mm_m M_w Mg Mp_m P] = model_oct_test(t,x,par,Emu,Ve2↩
    ,m_em2_tot,Win,cin,Tin,Tjin,Tr,Xi)
%% Measured data used in the model
index=floor(t/10)+1;
if index+1 < length(Tjin)
dt=(t-10*index)/10;
Tjin=dt*Tjin(index+1)+(1-dt)*Tjin(index);

else Tjin=Tjin(end);
end

index=floor(t/10)+1;
if index+1 < length(Tr)
dt=(t-10*index)/10;
Tr=dt*Tr(index+1)+(1-dt)*Tr(index);

else Tr=Tr(end);
end

index=floor(t/10)+1;
if index+1 < length(Xi)
dt=(t-10*index)/10;
Xi=dt*Xi(index+1)+(1-dt)*Xi(index);

else Xi=Xi(end);
end

%% Part II. Extract present value of states
Nini=x(1);              %Initiator left in reactor [mol]
Np=x(2);                %Number of particles [mol]
Nm=x(3);                %Monomer left in reactor [mol]
Nrad=x(4);              %Radicals in reactor [mol]
Tjout=x(5);             %Reactor jacket out temperature [K]
S=x(6);

%% Rate constants
[kp,ki,kt,ka,k_tr_mon,k_tr_CTA,k_tr_pol,kzp,kz_aq,Zp,Zaq]=rate_constant(par,Tr);

%% Part III. Intermediate calculations
Wc=((2.273*10^-13)*t^4)-((1.153*10^-8)*t^3)+((0.0001704)*t^2)-(0.6442*t)+6*10^4; %Flow rate↩
     of water inside the jacket [g/s]
mj=1000000;                     %Water in cooling jacket [g]

%Density, change with temperature in reactor (Kiparissides 1997).
[rho_m,rho_w,rho_p]=rho_PVC(Tr);

%Virial coefficients, from Kiparissides,w=water and m=monomer
[Bm,Bw,Bwm]=virial_coeff(Tr,par);
d_mw=2*Bwm-Bm-Bw;
```

```
%Emulgator into the reactor
m_em2=par.c_em2*m_em2_tot;                                    %Total amount of only ↩
    emulgator
m_em1=par.c_em1*par.m_em1_tot;                                %Total amount of only ↩
    emulgator [g]
n_em1=(m_em1/par.MWemu);                                      %Mol of emulgator
Ve1=par.m_em1_tot/rho_w;                                      %Emulgator feed into reactor, ↩
    model it as water (emulgator+water=water) [liter]
Vw=par.m_w/(rho_w)+Ve1+Ve2+(par.Buffer/rho_w);                %Volume of water in reactor [↩
    liter], surfactant used as water
m_w=par.m_w+m_em2_tot;                                        %Mass of water in reactor(↩
    Surfactant+buffer i model as water)
Vm0=(par.m_m)/rho_m;                                          %Initial volume of monomer in ↩
    reactor [liter]
Vi=par.m_i/par.rho_i;                                         %Initiator volume, per liter ↩
    water
as=10000;                                                     %Degree of coverage of the ↩
    surfactant

%Heat capacity (Kiparissides (1997))
cpm=(4.178*(18.67+(0.0758*(Tr-273.15))))/62.5;                %Heat capacity of monomer [J/g↩
    ,K]
cpw=4.02*exp((1.99*10^-4)*Tr);                                %Heat capacity of water   [J/g↩
    ,K]
cp_polymer=par.cp_polymer0;
m_m=par.MWm*Nm; m_p=par.m_m-(par.MWm*Nm);                     %Mass of monomer and polymer ↩
    in reactor [g]
mcp=(m_m*cpm)+((par.m_w+par.m_i+par.m_em1_tot+m_em2_tot)*cpw)+(m_p*cp_polymer); %Specific ↩
    heat capacity of reactor mixture [J/K]

%Mol of polymer particles, conversion and volume of reactor mixture
Mm=Nm*par.MWm;                                                %Mass of monomer left in ↩
    reactor [g]
N_polymer=par.Fm_in-Nm;                                       %Polymer in reactor [mol]
m_polymer=par.m_m-Mm;
X=(1-(Nm/par.Fm_in));                                         %Conversion
CTA=0;                                                        %Chain transfer agaent [mol/l]
frac_p=(m_polymer*rho_p)/(m_polymer*rho_p+rho_m*Mm);


[Pm_sat,Pw_sat] =saturation_pressure(Tr);

if X >= 0 && X <= 0.005
    kde=800;
elseif X > 0.005 && X <= 1
    kde=((5.189*10^4)*X^5) -((1.513*10^5)*X^4)+((1.553*10^5)*X^3) -((6.02*10^4)*X^2)+(1352*X)↩
        +3010;
 else
    kde=0;
end

%% Concentration of monomer in the polymer particles (two methods can be used)
%Simple method
[Mp,Vp]=monomer_concentration_particle(par,rho_m,rho_p,X);
% Monomer distribution in four phases (Flory-Huggins is used)
K1=0.0088;
%[Mp,Vp,Mm_m,M_w,Mg,Mp_m,P]=monomer_concentration_4phase(Nm,Tr,par,Pm_sat,Pw_sat,Bm,Bw,Bwm,↩
    rho_p,rho_w,rho_m,X,K1,m_polymer,Mm,d_mw,m_w);
```

```
%% Average number of radicals per particle
r_p=(150*10^-9)/2;  %Radius of a particle , assumed monodisperse
ap=4*pi*r_p^2;

vp = Vp / Np / par.Na;  %Volume of one particle

%Intermediate calculation for Np
a_Solvent = as * S;
a_Particles = (4*pi*Np*par.Na)^(1/3) * (0.003*Vp)^(2/3);
a_Miscelles = max( (a_Solvent-a_Particles), 0.0 );
ratefactor = a_Miscelles / a_Solvent;

jmax=5;                                                     %Jmax can be defined her

Nrw=( 2*ki*par.f_1*Nini*(1-ratefactor) + kde*Nrad )/((ka*Np*par.Na)+kde-(kz_aq*Zaq));

[para]=radicals_matrix(jmax,par,ka,kde,Nrw,Np,kt,kzp,Zp,vp, 2*par.f_1*ki*Nini*ratefactor);


Nrad_parti=Nrad-Nrw;
N_bar=Nrad_parti/Np;

% Polymerization rate
Rp=kp*Mp*Nrad_parti;                                        %(Nrad-Nrw): Radicals in ↩
    particles.
Tave=(Tjout+Tjin)/2;                                        %Average temperature in cooling ↩
    jacket

%Calculate U as a function of conversion
a0=5.166542937519126e+02;
a1=-5.383589032168123e+02;
a2=4.257394824341245e+02;
U=a0+a1*Xi+a2*Xi^2;
%% Part III. Evaluate ODE set
d_Nini = -ki*Nini;
d_Np   = 2 * par.f_1 * ki * Nini * ratefactor;
d_Nm   = -(Rp);
d_Nrad = 2*par.f_1*ki*Nini - kt/(vp*par.Na)*para - Nrad*(kzp*Zp-kz_aq*Zaq);
d_Tjout= (((Wc*cpw*(Tjin-Tjout))+(par.Ua*par.Aa*(par.Ta-Tjout))+(U*par.Ai*(Tr-Tave)))/((mj*↩
    cpw)+(par.m_met*par.cp_met)));
d_S    = Emu;

F=[d_Nini; d_Np; d_Nm; d_Nrad; d_Tjout; d_S];

end
```

B.2.3 Emulsion parameter file

```
function par =emulsion_parameters()
% ********** Constants and parameters for model ***********
%OTHER PARAMETERS
par.Vr=1;                     %Reactor volume [l]
par.Buffer=1;                 %Buffer put into reactor [g]
```

```
par.f_1=1;                    %Effeiciency factor for initiator
par.Na=6.022*10^23;           %Avogadros constant [molecules/mole]
par.R=8.314;                  %Gas constant [J/mole K]
par.xc=1;                     %Critical conversion, found from measured data
%HEAT CAPACITY
par.cp_polymer0=0.934;        %Heat capasity of reactor content [J/g K]
par.cpm0=0.9504;              %Heat capasity monomer [J/g K]
par.cpw0=4.187;               %Heat capacity of water [J/g K]
par.cp_emu=1;                 %Heat capacity of emulsifier in start
par.cpi0=1;                   %Heat capacity of initator
par.cp_met=1;                 %Heat capacity of steel [J/g,K]

%MOLECULAR WEIGHT
par.MWm=1;                    %Molecular weight of monomer [g/mole]
par.MWI=1;                    %Molecular weight of initiator [g/mole]
par.MWw=1;                    %Molecular weight of water [g/mole]
par.MWemu=1;                  %Molecular w of emulgator [g/mole]
par.Nmin=1;                   %Moles of monomer feed into the reactor
%DENSITY
par.rho_i=1;                  %Density of initiator [g/l]
par.rho_emu=1;                %Density of emulgator [g/l]


%FEED DATA
par.m_em1_tot=1;              %Emulgator nr 1 into reactor+water that the emulgator is ↩
    dissolved in [g]
par.c_em1=1;                  %Concentration emulgator 1 [%]
par.c_em2=1;                  %Concentration emulgator 2 [%]
par.Ta=1;                     %Temperature outside of the reactor, ambient temperature [K]
par.Fm_in=1;                  %Inlet of monomer into reactor [mole]
par.m_w=1;                    %Mass of water into reactor + buffer [g]
par.m_m=1;                    %Monomer put into the reactor [g]
par.m_i=1;                    %Initiator into the reactor [g]

%HEAT TRANSFER COEFFICIENTS AND AREA
par.deltaHp=1 ;               %Reaction entalpy for polymerization [J/mole]
par.Ut=1;                     %Top of reactor  [W/m2,K]
par.Ua=1;                     %heat transfer coefficient to the reactor environment [W/m2,K]
par.Ai=1;                     %Heat transfer area, jacket and reactor [m2]
par.A_t=1;                    %Reactor top heat transfer area [m2]
par.Aa=1;                     %Environmental heat transfer area, from jacket to environment ↩
    [m2]
par.m_met=1;                  %Data from Ineos, mass of steel [g]


%% ACTIVATION ENERGY, found in literature for each process.
par.Ep=60000; par.Et=4200; par.Ei=1;                       %[J/mol]
par.Ap=3.3*10^6; par.At=1.3*10^12;
par.kp0=52725; par.kt0=21*10^8; par.ki0=1;
par.Tref_I=343.15; par.Tref_p=323; par.Tref_t=333.15;


end
```

B.2.4 Rate constants

```
%**************************************************************************
% Name     : rate_constant
% Function : Use Arrhenius equation to calculate propagation, termination
% and initiation rate constant. A referance rate constant and temerature
% is used. Other rate constants are also given
% Author   : Anette H. Helgesen 2011
%**************************************************************************/
function [kp,ki,kt,ka,k_tr_mon,k_tr_CTA,k_tr_pol,kzp,kz_aq,Zp,Zaq]=rate_constant(par,Tr)

kp=(par.kp0*exp((-par.Ep/par.R)*((1/Tr)-(1/par.Tref_p))));

kt=(2*kp^2)/(((6.08*10^-3)/60)*exp(-5740*((1/Tr)-(1/par.Tref_t)))); %Literature value PVC

ki=par.ki0*exp((-par.Ei/par.R)*((1/Tr)-(1/par.Tref_I)));

ka=830;                      %Absorption of radicals [1/s]

%Transfer reactions rate and inhibitator data
k_tr_mon=0;                  %Transfer to monomer
k_tr_CTA=0;                  %Chain transfer agaent rate constant
k_tr_pol=0;                  %Transfer to polymer
kzp=0;                       %Inhibitator rate constant in particle [1/mol,s]
kz_aq=0;                     %Inhibitator rate constant in water [1/mol,s]
Zp=0;                        %Concentration of inhibitator in particle [mol/l]
Zaq=0;                       %Concentration of inhibitator in water    [mol/l]

end
```

B.2.5 Monomer concentration simple method

```
%*****************************************************************************
% Name     : monomer_concentration_particle
% Function : Calculate monomer concentration of monomer in particle, for
%            both interval II and III. Neglect monomer in gas and water
%            phase.
% Method   : Derived in this masterthesis
% Author   : Anette H. Helgesen
%*****************************************************************************/
function [Mp,Vp,P]=monomer_concentration_particle(par,rho_m,rho_p,X,Psat)

if X >= 0 && X <= par.xc
    phi_m=(1-par.xc)/(1-par.xc+(par.xc*(rho_m/rho_p)));

    Mp=(phi_m)*(rho_m/par.MWm);
    Vp=(par.Fm_in*par.MWm*X)*((1/rho_p)+((1/rho_m)*((1/par.xc)-1)));
    am=1;
    P=am*Psat;


elseif X > par.xc && X <= 1
    phi_m=(1-X)/(1-X+(X*(rho_m/rho_p)));

    Mp=(phi_m)*(rho_m/par.MWm);
    Vp=(par.Fm_in*par.MWm)*((X/rho_p)+((1-X)/rho_m));
```

```
    am=((1-Xi)/(1-par.xc))*(par.xc/Xi);
    P=am*Psat;
else
    disp(['ERROR: x ' num2str(X)]);
end
```

B.2.6 Monomer concentration with partition coefficients

```
%**************************************************************************
% Name     : monomer_partition
% Function : Calculate monomer concentration in polymer rich phase, by
% using partition coefficients. The calculations can be changed depending
% on which partition coefficient that is found for the system
% Ref      : Polymer Reaction Engineering, Jose Asua, 2007.
% Author   : Anette H. Helgesen 2011
%*************************************************************************/
function [Mp,Vpol,Vmd] = monomer_partition(par,Nm,rho_m,Vw)
Kaq_p=2; %Partition coefficient of monomer between the water and the particles
sigma=1; %Saturation degree of the particles
Vm=par.MWm*Nm/rho_m; %Volume of monomer left in reactor

Mc=Nm/Vm; %Monomer concentration in reactor mixture, from MB. Nm/Vm

%%Equation that have to be solved
Kd_aq=sigma/Kaq_p;
Vm_aq=Vw/Kd_aq;
Vp=(Kaq_p*(Vm-Vm_aq)*Vw)/Vm_aq; %Overall volume of particles
Vmp=Vm-Vw;
Vpol=Vp-Vmp;
Vmd=(Mc*V*(par.MWm/rho_m))-Vm_aq-Vmp;

Mp=(Vmp*rho_m)/(Vp*par.MWm);
end
```

B.2.7 Monomer distribution in four phase

```
%*****************************************************************************
% Name     : monomer_concentration_4phase
% Function : Calculate monomer concentration of monomer in water,
%            monomer rich phase, gas phase and polymer rich phase. For
%            both interval II and III.
% Method   : Ref: Kiparissides et al., 1997, Ind.Eng. Chem. Res. Page 1266
%            Ref: Mejdell et al., 1999, Chem.Eng Science 54. Page
%            2459-2466
% Author   : Anette H. Helgesen 2011
%****************************************************************************/
function[Mp,Vp,Mm_m,M_w,Mg,Mp_m,P]=monomer_concentration_4phase(Nm,Tr,par,Pm_sat,Pw_sat,Bm,↩
    Bw,Bwm,rho_p,rho_w,rho_m,X,K1,m_polymer,Mm,d_mw,m_w)

k=1000;
```

```
    delta=1/(1+exp(k*(X-par.xc)));

    P1=(Pm_sat+Pw_sat)*1;                          %[PA]
    am = 1.0;                                      %Activity monomer
    para_f1=Flory(Tr,am);                          %Polymer volume fraction

    ym=1-(Pw_sat/P1);
    yw=1-ym;
    B_1=Bm+((yw^2)*((2*Bwm)-Bm-Bw));               %Virial coefficient [m3/mole]
    fm_g=ym*P1*exp((B_1*P1)/(par.R*1000*Tr));      %Fugasity [Pa]
    fw_g=P1-fm_g;                                  %Fugasity of water in gas phase [Pa]

    B_2=((ym^2)*Bm^2)+(2*ym*yw*Bwm)+((yw^2)*Bw);
    z=1+((B_2*P1)/(par.R*1000*Tr));
    Vg=(par.Vr-(par.m_m/rho_m)-(m_w/rho_w)+(par.m_m*X*((1/rho_m)-(1/rho_p))))/(1-((P1/(z*par↩
        .R*Tr))*(((ym*par.MWm)/(rho_p*1000))+(((yw*par.MWw))/(rho_w*1000))))); % Volume of ↩
        gas phase [liter]

    Vg1=Vg/1000;                                   %[m3]
    Mg1=(par.MWm*ym*Vg1*P1)/(z*par.R*Tr);          %[g]
    Wg1=(par.MWw*yw*Vg1*P1)/(z*par.R*Tr);
    M_w1=(K1*(Pm_sat/P1))*(par.m_w-Wg1);           %[g]

    xs=(para_f1*rho_p)/((para_f1*rho_p)+((1-para_f1)*rho_m));
    Mm_m1=(par.m_m*((1-(X/xs))))-M_w1-Mg1;         %mass of monomer in monomer phase[g]
    Mp_m1=(par.m_m*(((X+(1e-20))/xs)))*(1-xs);     %mass of monomer in polymer rich phase [g]
    Vp1=(Mp_m1/rho_m)+((par.m_m*(X))/rho_p);       %Volume of polymer particle [l]
    Mp1=Mp_m1/(par.MWm*Vp1);                       %Concentration of monomer in polymer ↩
        particle [mole/l]


if (Mm_m1 <= 0);
    Mm_m1=0;

end
    para_f1 =(m_polymer*rho_p)/((m_polymer*rho_p)+(Mm*rho_m));

    am=florytest2(para_f1,Tr);
    fm0=Pm_sat*exp((Bm*Pm_sat)/(par.R*1000*Tr));

    global gx0
     options=optimset('Display','off','TolFun',1e-06);
     if isempty(gx0)
        gx0=600000;
     end
    P2=fsolve(@pressure,gx0,options,Pw_sat,Tr,Bm,d_mw,fm0,am,par);
    gx0=P2;
    % Can also use:
    %P2=(Pm_sat+Pw_sat)*am;

    ym=1-(Pw_sat/P2);
    yw=1-ym;
    xs=(para_f1*rho_p)/((para_f1*rho_p)+((1-para_f1)*rho_m));
    B_1=Bm+((yw^2)*((2*Bwm)-Bm-Bw)); %[m3/mole]
    fm_g=ym*P2*exp((B_1*P2)/(par.R*1000*Tr));
    fw_g=P2-fm_g;

    B_2=((ym^2)*Bm^2)+(2*ym*yw*Bwm)+((yw^2)*Bw);
```

```
    z=1+((B_2*P2)/(par.R*1000*Tr));

    Vg=(par.Vr-(par.m_m/rho_m)-(m_w/rho_w)+(par.m_m*par.xc*((1/rho_m)-(1/rho_p))))/(1-((P1/(↩
        z*par.R*Tr))*(((ym*par.MWm)/(rho_p*1000))+(((yw*par.MWw))/(rho_w*1000))))); % Volume↩
         of gas phase [liter]
    Vg1=Vg/1000; %Have to make volume into m3

    Mg2=(par.MWm*ym*Vg1*P2)/(z*par.R*Tr);        %[g]
    Wg2=(par.MWw*yw*Vg1*P2)/(z*par.R*Tr);        %[g]
    M_w2=(K1*(Pm_sat/P2))*(par.m_w-Wg2);         %[g]
    Mp_m2=(par.m_m*(1-X))-M_w2-Mg2;              %[g]
    Vp2=(Mp_m2/rho_p)+(par.m_m*(X+1e-08)/rho_p); %[l]
    Mp2=Mp_m2/(par.MWm*Vp2);                     %[mole/l]
    Mm_m2=0;

    Mp=((delta)*Mp1)+((1-delta)*Mp2);
    Vp=((delta)*Vp1)+((1-delta)*Vp2);
    P=((delta)*P1)+((1-delta)*P2);
    Mm_m=((delta)*Mm_m1)+((1-delta)*Mm_m2);
    M_w=((delta)*M_w1)+((1-delta)*M_w2);
    Mg=((delta)*Mg1)+((1-delta)*Mg2);
    Mp_m=((delta)*Mp_m1)+((1-delta)*Mp_m2);
```

Saturation pressure

```
%*****************************************************************
% Name      : saturation_pressure
% Function  : Give vapour pressure as a function of temperature
% Author    : Anette H. Helgesen 2011
% Referance: Kiparissides (1997)
%*****************************************************************

function [Pm_sat,Pw_sat] = saturation_pressure(Tr)
%               Out: Sat. pressure for VCM [Pa]
%               In: temperature            [K]
Pw_sat=exp(72.55-(7206.7/Tr)-(7.1386*log(Tr))+((4.046*10^-6)*Tr^2));
Pm_sat=exp(126.85-(5760.1/Tr)-(17.914*log(Tr))+((2.4917*10^-2)*Tr));
```

Pressure in interval III

```
%*************************************************************************
% Name      : pressure
% Function  : Calculate pressure in interval III.
% Method    : Ref: Kiparissides et al., 1997, Ind.Eng. Chem. Res. P. 1258
% Author    : Anette H. Helgesen
%*************************************************************************
function F = pressure(P,Pw_sat,Tr,Bm,d_mw,fm_0,am,par)

F=((P-Pw_sat)*(exp((P/(par.R*1000*Tr))*(Bm+((Pw_sat/P)^2)*d_mw))))-fm_0*am;

end
```

Density

```
%*******************************************************************************
%  Name      : density_process
%  Function  : Calculate density of water, monomer and PVC as a function of temperature
%              this can be changed, but PVC is used as this is form the case
%  Referance: Kiparissides (1997)
%  Author    : Anette H. Helgesen 2011
%*******************************************************************************/

function [rho_m,rho_w,rho_p] = density_process(Tr)
%                Out: Sat. pressure for VCM [Pa]
%                In:  Temperature          [K]
rho_m=947.1-(1.746*(Tr-273.15))-((3.24*10^-3)*(Tr-273.15)^2); %Density of monomer [g/l] (↩
    Constant value 911)
rho_p=(10^3)*exp(0.4296-(3.274*10^-4)*Tr);                      %Density of polymer [g/l] (↩
    Constant value 1392)
rho_w=1011-(0.4484*(Tr-273.15));                                %Density of water [g/l] (↩
    Constant value 1000)
```

Virial coefficients

```
%*************************************************************************
%  Name      : virial_coeff
%  Function  : Calculate virial coefficients. Values used are for PVC
%  production.
%  Method    : Ref: Kiparissides et al., 1997, Ind.Eng. Chem. Res. Page 1266
%  Author    : Anette H. Helgesen 2011
%*************************************************************************/
function [Bm,Bw,Bwm] = virial_coeff(Tr,par)
w_w=0.3342; w_m=0.1048;        %[-]
Tc_w=647.5; Tc_m=432;          %[K]
Pc_w=220.5e05; Pc_m=56e05;     %[Pa]
Vc_w=56;    Vc_m=179;          %[cm3/mol]
Zc_w=0.233; Zc_m=0.283;        %[-]

Tr_w=Tr/Tc_w;                  %[K]
Tr_m=Tr/Tc_m;                  %[K]

Bm_0=0.083-(0.422/(Tr_m^(1.6)));
Bm_1=0.139-(0.172/(Tr_m^(4.2)));
Bm=((par.R*1000*Tc_m)/Pc_m)*(Bm_0+w_m*Bm_1); %[m3/mol]

Bw_0=0.083-(0.422/(Tr_w^(1.6)));
Bw_1=0.139-(0.172/(Tr_w^(4.2)));
Bw=((par.R*1000*Tc_w)/Pc_w)*(Bw_0+w_w*Bw_1); %[m3/mol]

w_wm=(w_w+w_m)/2;
Tc_wm=((Tc_w*Tc_m)^(0.5));
Zc_wm=(Zc_w+Zc_m)/2;
Vc_wm=((((Vc_w^(1/3))+(Vc_m^(1/3)))^3)/2)/1000;
%Pc_wm=((Zc_wm*par.R*1000*Tc_wm)/(Vc_wm))
Pc_wm = 107.e5;
```

```
Tr_wm=Tr/Tc_wm;

Bwm_0=0.083-(0.422/(Tr_wm^(1.6)));
Bwm_1=0.139-(0.172/(Tr_wm^(4.2)));
Bwm=((par.R*Tc_wm)/Pc_wm)*(Bwm_0+w_wm*Bwm_1); %[m3/mol]
```

Flory-Huggins equation

```
%***************************************************************************
% Name       : Flory
% Function   : Computes the volume fraction of polymer in the polymer phase
% Method     : Solves the Flory Huggins equation for PVC
%              Ref: Kiparissides et al., 1997, Ind.Eng. Chem. Res., 36,1253-1267.
% Author     : Peter Singstad    2004-03-21
% Rewritten: Peter Singstad    2005-03-03
% Modified:  Peter Singstad    2008-01-13
%***************************************************************************
function vf = Flory(Tr,am)

[c4, c3, c2, c1, c0 ] = coeffFlory(Tr,am);

x = 1.0 - 0.25 .* am * am * am .* ( 1.0 + (Tr-323.15) ./ 500 );

for i=1:4,
   r = log(1-x) + (((c4 .* x + c3) .* x + c2 ) .* x + c1 ) .* x + c0;
   dr = 1./(x-1) + (( 4*c4 .* x + 3*c3) .* x + 2*c2 ) .* x + c1;

   x = x - r ./ dr;
end

vf = x;
```

```
%****************************************************************************
% Name       : CoeffFlory
% Function   : Returns parameters for Flory-Huggins equation for PVC. This
% is used to find the interaction parameter and the polymer volume
% fraction in the polymer rich phase. If the parameters are changed,
% this can be used for other processes.
% Method     : Ref: Kiparissides et al., 1997, Ind.Eng. Chem. Res. Page 1266
% Author     : Peter Singstad and Anette H. Helgesen
%****************************************************************************/
function [c4, c3, c2, c1, c0] = coeffFlory(Tr,am)

    Xs   = 0.26;
    a    = 0.15524;
    b    = 0.35311;
    c    = -0.50527;
    d    = 11.3605;
    e    = 199.96;             %This is from V1*(d1-d2)^2/R [K]
    f    = 6244.49;            %This is from 2*d1*d2/R [K]

   c4 = f * b / Tr;
   c3 = f * c / Tr;
```

```
    c2 = Xs + e/Tr + f*a/Tr + f*d/(Tr*Tr);
    c1 = 1.0;
    c0 = - log( am );
```

```
%****************************************************************************
% Name     : Flory_III
% Function : Use Flory-Huggins equation to calculate activity in interval
% III.
% Method   : Ref: Kiparissides et al., 1997, Ind.Eng. Chem. Res. Page 1266
% Author   : Anette H. Helgesen
%****************************************************************************/
function am=floryIII(para_f1,Tr)

Xs  = 0.26;
    a   = 0.15524;
    b   = 0.35311;
    c   = -0.50527;
    d   = 11.3605;
    e   = 199.96;              %This is from V1*(d1-d2)^2/R [K]
    f   = 6244.49;             %This is from 2*d1*d2/R [K]

 am=(exp(log(1-para_f1)+para_f1+((Xs+(e/Tr)+((f/Tr)*(a+(b*para_f1^2)+(c*para_f1)+(d/Tr))))*↩
     para_f1^2)));
```

B.2.8 Radical distribution in the polymer particles

N(j) solved as states

```
%****************************************************************************
% Name     : model_radicals_states
% Function : Solves moles of particles with 0,1,2,--- radicals as states
% Method   : Metod that solves the equations without assuming steady state
% Author   : Anette Hoel Helgesen 2011
%****************************************************************************/
function [F n_bar X N_polymer Rp Mp Np] = model_radicals_states(t,x,par,Emu,Ve2,m_em2_tot,↩
    Win,cin,Tin,Tjin,Tr,Xi)
%% Process data from Ineos.
index=floor(t/10)+1;
if index+1 < length(Tjin)
dt=(t-10*index)/10;
Tjin=dt*Tjin(index+1)+(1-dt)*Tjin(index);

else Tjin=Tjin(end);
end

index=floor(t/10)+1;
if index+1 < length(Tr)
dt=(t-10*index)/10;
Tr=dt*Tr(index+1)+(1-dt)*Tr(index);

else Tr=Tr(end);
end
```

```
index=floor(t/10)+1;
if index+1 < length(Xi)
dt=(t-10*index)/10;
Xi=dt*Xi(index+1)+(1-dt)*Xi(index);

else Xi=Xi(end);
end

%% Part II. Extract present value of states
Nini=x(1);              %Initiator left in reactor [mole]
Nm=x(2);                %Monomer left in reactor [mole]
Tjout=x(3);             %Reactor jacket out temperature [K]
S=x(4);                 %Surfactant [mole]
N1=x(5);                %Moles of particles with 0 radical
N2=x(6);                %Moles of particles with 1 radical
N3=x(7);                %Moles of particles with 2 radicals
N4=x(8);                %Moles of particles with 3 radicals
N5=x(9);                %Moles of particles with 4 radicals
%% Rate constants
[kp,ki,kt,ka,k_tr_mon,k_tr_CTA,k_tr_pol,kzp,kz_aq,Zp,Zaq]=rate_constant(par,Tr);

%% Part III. Intermediate calculations
Wc=((2.273*10^-13)*t^4)-((1.153*10^-8)*t^3)+((0.0001704)*t^2)-(0.6442*t)+6.0*10^4;  %Flow ↩
    rate of water inside the jacket [g/s]
mj=1000000;    %Water in cooling jacket [g]

%Density, change with temperature in reactor (Kiparissides 1997).
[rho_m,rho_w,rho_p]=density_prcess(Tr);

%Virial coefficients, from Kiparissides,w=water and m=monomer
[Bm,Bw,Bwm]=virial_coeff(Tr,par);
d_mw=2*Bwm-Bm-Bw;

%Emulgator into the reactor, find concentration of the emulgator
m_em2=par.c_em2*m_em2_tot;                             %Total amount of only ↩
    emulgator
m_em1=par.c_em1*par.m_em1_tot;                         %Total amount of only ↩
    emulgator [g]
n_em1=(m_em1/par.MWemu);                               %Mol of emulgator
Ve1=par.m_em1_tot/rho_w;                               %Emulgator feed into reactor, ↩
    model it as water (emulgator+water=water) [liter]


% Heat capacity (Kiparissides (1997))
cpw=4.02*exp((1.99*10^-4)*Tr);                         %Heat capacity of water  [J/g↩
    ,K]

%Mol of polymer particles, conversion and volume of reactor mixture
Mm=Nm*par.MWm;                                         %Mass of monomer left in ↩
    reactor [g]
N_polymer=par.Fm_in-Nm;                                %Polymer in reactor [mol]
m_polymer=par.m_m-Mm;
X=(1-(Nm/par.Fm_in));                                  %Conversion

%This is estimated for Mp simple method and xc found from measured data
if X >= 0 && X <= 0.005
    kde=800;
```

```
elseif X > 0.005 && X <= 1
    kde=((5.189*10^4)*X^5)-((1.513*10^5)*X^4)+((1.553*10^5)*X^3)-((6.02*10^4)*X^2)+(1352*X)↩
        +3010;
 else
    kde=0;
end

[Pm_sat,Pw_sat]=sat_pressure(Tr);
Psat=Pm_sat+Pw_sat;
%% Monomer in particle
[Mp,Vp,P]=monomer_concentration_particle(par,rho_m,rho_p,X,Psat);

%% Average number of radicals per particle
r_p=(150*10^-9)/2;                                          %Radius of a particle, assumed ↩
    monodisperse
Np=N1+N2+N3+N4+N5;
vp = Vp / Np / par.Na;
%% Solve a DAE system for radicals per partciel
n_bar=(0*N1+1*N2+2*N3+3*N4+4*N5)/Np;

Nrw=((2*ki*par.f_1*Nini)+(kde*Np*n_bar))/(ka*Np*par.Na);

% Polymerization rate
Rp=kp*Mp*n_bar*Np;
Tave=(Tjout+Tjin)/2;               %Average temperature in cooling jacket

%Heat transfer parameters
a0=5.166542937519126e+02;
a1=-5.383589032168123e+02;
a2=4.257394824341245e+02;

U=a0+a1*Xi+a2*Xi^2;

%% Part III. Evaluate ODE set
d_Nini = -ki*Nini;
d_Nm   = -(Rp);
d_Tjout= (((Wc*cpw*(Tjin-Tjout))+(par.Ua*par.Aa*(par.Ta-Tjout))+(U*par.Ai*(Tr-Tave)))/((mj*↩
    cpw)+(par.m_met*par.cp_met)));
d_S    = Emu;

d_N0=-(ka*Nrw*N1*par.Na)+(2*(kt/(par.Na*vp))*N3)+(kde*N2); %N0
d_N1=((ka*Nrw*par.Na)*(N1-N2))+(6*(kt/(par.Na*vp))*N4)-(kde*(N2-2*N3)); %N1
d_N2=((ka*Nrw*par.Na)*(N2-N3))-(kde*(2*N3-(3*N4)))+((kt/(vp*par.Na))*(12*N5-(2*N3))); %N2
d_N3=((ka*Nrw*par.Na)*(N3-N4-N5))-((kt/(vp*par.Na))*(6*N4))-(kde*(3*N4-(4*N5))); %N3
d_N4=((ka*Nrw*par.Na)*(N4+N5))-((kt/(vp*par.Na))*(12*N5))-(kde*4*N5); %N=4


F=[d_Nini; d_Nm; d_Tjout; d_S; d_N0; d_N1; d_N2; d_N3; d_N4];


end
```

The new way derived in this thesis

In the main model given, moles of radicals are solved as steady state and total moles of radicals are a state. The maximum number of radicals per particles has to be given in the *main_model.m*.

J_{max}=free to choose.

```
%************************************************************************
% Name      : radicals_matrix
% Function  : Linear equation set from all populations balances are solved.
% Number of moles of particles with zero, one, two, etc. radicals are
% found. (In this matlab file, jmax=5 is actually jmax=4)
% Method    : This method is found and derive in this masterthesis
% Author    : Anette H. Helgesen 2011
%************************************************************************/
function [para mat]=radicals_matrix(jmax,par,ka,kde,Nrw,Np,kt,kzp,Zp,vp,rp)
A=zeros(jmax,jmax);
%The first row, for j=0
A(1,1)=1; A(1,2)=1; A(1,3)=1; A(1,4:jmax)=1;
%Second row, for j=1
A(2,1)=(ka*Nrw*par.Na); A(2,2)=-(ka*Nrw*par.Na)-((kzp*Zp)+kde); A(2,3)=2*((kzp*Zp)+kde); A↩
    (2,4)=6*(kt/(par.Na*vp)); A(2,5:jmax)=0; % ok

for i=3:jmax-2

    A(i,i-1)=(ka*Nrw*par.Na);
    A(i,i)=(-(ka*Nrw*par.Na))-((kt/(par.Na*vp))*(i-1)*(i-2))-(((kzp*Zp)+kde)*(i-1));
    A(i,i+1)=((kzp*Zp)+kde)*(i);
    A(i,i+2)=(kt/(par.Na*vp))*(i+1)*(i);

end
%for jmax-1
A(jmax-1,jmax-2)=(ka*Nrw*par.Na);
A(jmax-1,jmax-1)=-((ka*Nrw*par.Na))-((kt/(vp*par.Na))*(jmax-2)*(jmax-3))-(((kzp*Zp)+kde)*(↩
    jmax-2));
A(jmax-1,jmax)=-((ka*Nrw*par.Na))+(((kzp*Zp)+kde)*(jmax-1));

%for jmax
A(jmax,jmax-1)=(ka*Nrw*par.Na);
A(jmax,jmax)=(ka*Nrw*par.Na)-((kt/(par.Na*vp))*(jmax-1)*(jmax-2))-(((kzp*Zp)+kde)*(jmax-1));

%The b matrix
b=zeros(jmax,1); b(1) = Np; b(2)=rp;

%C matrix used for the termination term when finding number of radicals
IMAX=jmax-2;
IMIN=3;
c= zeros(1,IMAX-IMIN+1);
for i=IMIN:IMAX
c(i-IMIN+1)=i*(i+1);
end
c =2*[0 0 2 6 c];
mat=A\b;
para=c*(A\b);
```

Zero-one system

```
%************************************************************************
```

```
% Name     : model_zero_one_system
% Function : Assume all particles have zero or one radical.
% Method   : Simple method derived in this work.
% Author   : Anette Hoel Helgesen 2011
%*************************************************************************/
function [F X N1 N0] = model_zero_one_system(t,x,par,Emu,Ve2,m_em2_tot,Win,cin,Tin,Tjin,Tr,↩
    Xi)
%% Process data from Ineos. Data made to polynomials.
index=floor(t/10)+1;
if index+1 < length(Tjin)
dt=(t-10*index)/10;
Tjin=dt*Tjin(index+1)+(1-dt)*Tjin(index);

else Tjin=Tjin(end);
end

index=floor(t/10)+1;
if index+1 < length(Tr)
dt=(t-10*index)/10;
Tr=dt*Tr(index+1)+(1-dt)*Tr(index);

else Tr=Tr(end);
end

index=floor(t/10)+1;
if index+1 < length(Xi)
dt=(t-10*index)/10;
Xi=dt*Xi(index+1)+(1-dt)*Xi(index);

else Xi=Xi(end);
end

%% Part II. Extract present value of states
Nini=x(1);              %Initiator left in reactor [mole]
Np=x(2);                %Number of particles [mole]
Nm=x(3);                %Monomer left in reactor [mole]
Tjout=x(4);             %Reactor jacket out temperature [K]
S=x(5);
%% CONSTANTS that are unknown, have to be/should be estimated
[kp,ki,kt,ka,k_tr_mon,k_tr_CTA,k_tr_pol,kzp,kz_aq,Zp,Zaq]=rate_constant(par,Tr);

%% Part III. Intermediate calculations
Wc=((2.273*10^-13)*t^4)-((1.153*10^-8)*t^3)+((0.0001704)*t^2)-(0.6442*t)+6*10^4;  %Flow rate↩
    of water inside the jacket [g/s]
mj=1000000;                         %Water in cooling jacket [g]

%Density, change with temperature in reactor (Kiparissides 1997).
[rho_m,rho_w,rho_p]=rho_PVC(Tr);
%Virial coefficients, from Kiparissides,w=water and m=monomer
[Bm,Bw,Bwm]=virial_coeff(Tr,par);
d_mw=2*Bwm-Bm-Bw;

%Emulgator into the reactor, find concentration of the emulgator
m_em2=par.c_em2*m_em2_tot;                               %Total amount of only ↩
    emulgator
m_em1=par.c_em1*par.m_em1_tot;                           %Total amount of only ↩
    emulgator [g]
n_em1=(m_em1/par.MWemu);                                 %Mol of emulgator
```

```
Ve1=par.m_em1_tot/rho_w;                                    %Emulgator feed into reactor, ↩
    model it as water (emulgator+water=water) [liter]
Vw=par.m_w/(rho_w)+Ve1+Ve2+(par.Buffer/rho_w);              %Volume of water in reactor [↩
    liter], surfactant used as water
Vm0=(par.m_m)/rho_m;                                        %Initial volume of monomer in ↩
    reactor [liter]
Vi=par.m_i/par.rho_i;                                       %Initiator volume, per liter ↩
    water
Vw=par.m_w/(rho_w)+Ve1+Ve2+(par.Buffer/rho_w);              %Volume of water in reactor [↩
    liter], surfactant used as water
as=10;                                                      %Å2/molecule
m_w=par.m_w+m_em2_tot;                                      %Mass of water in reactor(↩
    Surfactant+buffer i model as water)



% Heat capacity (Kiparissides (1997))
cpm=(4.178*(18.67+(0.0758*(Tr-273.15))))/62.5;              %Heat capacity of monomer [J/g↩
    ,K]
cpw=4.02*exp((1.99*10^-4)*Tr);                              %Heat capacity of water  [J/g↩
    ,K]
cp_polymer=par.cp_polymer0;
m_m=par.MWm*Nm; m_p=par.m_m-(par.MWm*Nm);                  %Mass of monomer and polymer in↩
     reactor [g]
mcp=(m_m*cpm)+((par.m_w+par.m_i+par.m_em1_tot+m_em2_tot)*cpw)+(m_p*cp_polymer); %Specific ↩
    heat capacity of reactor mixture [J/K]

%Mol of polymer particles, conversion and volume of reactor mixture
Mm=Nm*par.MWm;                                              %Mass of monomer left in ↩
    reactor [g]
N_polymer=par.Fm_in-Nm;                                     %Polymer in reactor [mol]
m_polymer=par.m_m-Mm;
X=(1-(Nm/par.Fm_in));                                       %Conversion
CTA=0;                                                      %Chain transfer agaent [mol/l]
frac_p=(m_polymer*rho_p)/(m_polymer*rho_p+rho_m*Mm);

[Pm_sat,Pw_sat] =sat_pressure(Tr);
Psat=Pm_sat+Pw_sat;
%% Monomer in polymer rich phase
[Mp,Vp,P]=monomer_concentration_particle(par,rho_m,rho_p,X,Psat);

%% Monomer distribution in four phases (Flory-Huggins is used)
K1=0.0088;
%[Mp,Vp,Mm_m,M_w,Mg,Mp_m,P]=monomer_concentration_4phase(Nm,Tr,par,Pm_sat,Pw_sat,Bm,Bw,Bwm,↩
    rho_p,rho_w,rho_m,X,K1,m_polymer,Mm,d_mw,m_w);

%% Average number of radicals per particle
r_p=(150*10^-9)/2; %Radius of a particle, assumed monodisperse (given from Ineos)

kde=100;
vp = Vp / Np / par.Na;

a_Solvent = as * S;
a_Particles = (4*pi*Np*par.Na)^(1/3) * (0.003*Vp)^(2/3);
a_Miscelles = max( (a_Solvent-a_Particles), 0.0 );
ratefactor = a_Miscelles / a_Solvent;

N1=quadratic_equation(par,ki,Nini,ka,Np,kde,kt,vp);
```

```
Nrw=(par.f_1*ki*Nini)/(ka*par.Na*N1);

% Polymerization rate
Rp=(kp*Mp*N_bar*Np);
Tave=(Tjout+Tjin)/2; %Average temperature in cooling jacket

%Possible to calculate U, to see how it change
a0=5.166542937519126e+02;
a1=-5.383589032168123e+02;
a2=4.257394824341245e+02;

U=a0+a1*Xi+a2*Xi^2;
%% Part III. Evaluate ODE set
d_Nini = -ki*Nini;
d_Np   = 2 * par.f_1 * ki * Nini * ratefactor;
d_Nm   = -(Rp);
d_Tjout= (((Wc*cpw*(Tjin-Tjout))+(par.Ua*par.Aa*(par.Ta-Tjout))+(U*par.Ai*(Tr-Tave)))/((mj*↩
    cpw)+(par.m_met*par.cp_met)));
d_S    = Emu;

F=[d_Nini; d_Np; d_Nm; d_Tjout; d_S];

end
```

B.2.9 Moment balances

This sub-model have to be included with the mass and enegy balances, and off course other nessasary intermediate calculation.

```
%*************************************************************************
% Name      : moment_equations
% Function : Moment equations, this have to be included with mass and
% energy balances. And other intermediate calculation nessasary.
% Author   : Anette H. Helgesen 2011
%*************************************************************************/
function [F]=moment_equations(t,x,par)
%% Part  II. Extract present value of states
p0=x(1);
p1=x(2);
p2=x(3);
m0=x(4);
m1=x(5);
m2=x(6);
%% Rate constants and other kinetic parameters
[kp,ki,kt,ka,k_tr_mon,k_tr_CTA,k_tr_pol,kzp,kz_aq,Zp,Zaq]=rate_constant(par,Tr);

MW_n=(m1/m0)*par.MWm;
MW_w=(m2/m1)/par.MWm;
PDI=(MW_w)/(MW_n);


%% III: States
dx1=(2*par.f_1*ki*I)-(kt*p0^2);
```

```
dx2=(2*par.f_1*ki*I)+(k_tr_mon*M*p0)+(k_tr_CTA*CTA*p0)+(kp*M*p0) -(((k_tr_mon*M)+(k_tr_CTA*↩
    CTA)+(kt*p0))*p1)+(k_tr_pol*((p0*m2)-(p1*m1)));
dx3=(2*par.f_1*ki*I)+(k_tr_mon*M*p0)+(k_tr_CTA*CTA*p0)+(kp*M*(p0+2*p1)) -(((k_tr_mon*M)+(↩
    k_tr_CTA*CTA)+(kt*p0))*p2)+(k_tr_pol*((p0*(m2/(m0*m1))*((2*m0*m1)-m1^2))-(p2*m1)));
dx4=(k_tr_mon*M*p0)+(k_tr_CTA*CTA*p0)+(kt*(p0+0.5*p0));
dx5=(((k_tr_mon*M)+(k_tr_CTA)+kt*p0)*p1)+(k_tr_pol*((p1*m1)+(p0*m2)));
dx6=(((k_tr_mon*M)+(k_tr_CTA)+kt*p0)*p2)+(ktc*p1^2)+(k_tr_pol*((p2*m1)+(p0*(m2/(m0*m1))*((2*↩
    m0*m1)-m1^2))));

F=[dx1;dx2;dx3;dx4;dx5;dx6];
end
```

B.2.10 Estimation of parameters with *lsqcurvefit*

To avoid to include to much, only the m-files for estimation of the heat-transfer coefficient will be include.

```
%**************************************************************************
% Name     : main_curvefit_U
% Function : Main file to run the lsqcruvefit
% Method   : Load data that is used as ydata, and compared with model
% Author   : Anette Hoel Helgesen 2011
% %**********************************************************************/
load data
par = emulsion_parameters();

xdata=[0:10:31620]';
Nineos=data((359:3521),2)/100; %(ydata)
param0=[100 100 100];
options = optimset('TypicalX',[1 1 1],'MaxIter',1e3,'MaxFunEvals',1000,'TolFun',1e-15,'TolX'↩
    ,1e-15);
[x,resnorm,residual,exitflag,output]=lsqcurvefit(@main_estimation_U_ode15s,param0,xdata,↩
    Nineos,[],[],options);
```

```
%********************************************************************************
% Name     : main_estimation_U_ode15s
% Function : Used to run lsqcruvefit, to estimate parameters
% Method   : Use ode15s, stiff ode solver
% Author   : Anette Hoel Helgesen 2011
% %****************************************************************************/
function res=main_estimation_U_ode15s(par,xdata)

a0=par(1);
a1=par(2);
a2=par(3);

load data
par = emulsion_parameters();
%% Timespan and states
tspan=xdata;
times=[];
States=[];
```

```
%% Initial values for the states.
x10=[359];
options=odeset('BDF','on','AbsTol',1e-6,'RelTol',1e-6); %,'maxStep',0.0001
format('shortG')
Tr=data((359:3521),7)+273.15;
Tjin=data((359:3521),5)+273.15;
Xi=data((359:3521),2)/100;
%% ODE solver
%After dosing of emulgator, but not in this interval of the batch time
[T,x1]= ode15s(@estimation_U,tspan,x10,options,par,Emu,Ve2,m_em2_tot,Win,cin,Tin,Tjin,Tr,Xi,↩
    a0,a1,a2);
times=[times;T];
States=[States;x1];
res=States(:,1);
end
```

```
%**********************************************************************
% Name     : estimation_U
% Function : Model used to estimate U
% Method   : Estimate U with lsqcruvefit, have to run the model
% Author   : Anette H. Helgesen 2011
%**********************************************************************
function F =estimation_U(t,x,par,Emu,Ve2,m_em2_tot,Win,cin,Tin,Tjin,Tr,Xi,a0,a1,a2)
%% Data used in model
index=floor(t/10)+1;
if index+1 < length(Tjin)
dt=(t-10*index)/10;
Tjin=dt*Tjin(index+1)+(1-dt)*Tjin(index);

else Tjin=Tjin(end);
end

index=floor(t/10)+1;
if index+1 < length(Tr)
dt=(t-10*index)/10;
Tr=dt*Tr(index+1)+(1-dt)*Tr(index);

else Tr=Tr(end);
end

index=floor(t/10)+1;
if index+1 < length(Xi)
dt=(t-10*index)/10;
Xi=dt*Xi(index+1)+(1-dt)*Xi(index);

else Xi=Xi(end);
end

% Water flow in cooling jacket.
Wc=((2.273*10^-13)*t^4)-((1.153*10^-8)*t^3)+((0.0001704)*t^2)-(0.6442*t)+6*10^4;
%% Part II. Extract present value of states
Tjout=x(1);                   %Reactor jacket out temperature [K]
%% Part III. Intermediate calculations
mj=100000;                    %Water in cooling jacket [g]
cpw=4.02*exp((1.99*10^-4)*Tr); %Heat capacity of water   [J/g,K]
Tave=(Tjout+Tjin)/2;          %Average temperature in cooling jacket
```

```
U=a0+a1*Xi+a2*Xi^2;
%% Part III. Evaluate ODE set
dx1=(((Wc*cpw*(Tjin-Tjout))+(par.Ua*par.Aa*(par.Ta-Tjout))+(U*par.Ai*(Tr-Tave)))/((mj*cpw)+(↩
    par.m_met*par.cp_met)));
F=dx1;

end
```

Appendix C

Risk assessment

NTNU	Risk assessment	Prepared by	Number	Date	
		HSE section	HMSRV-26/03	01.12.2006	
		Approved by	Page	Replaces	
HSE/KS		The Rector	1 out of 2	15.12.2003	

Unit: Chemical Engineering **Date: 30.05.2011**

Line manager: Øyvind Gregeresen

Participants in the risk assessment (including their function): Anette Hoel Helgesen

Activity from the identification process form	**Potential undesirable incident/strain**	**Likelihood:**	**Consequence:**			**Risk value**	**Comments/status Suggested measures**
		Likelihood (1-4)	Human (1-4)	Environment (1-4)	Economy/ materiel (1-4)		
Working with PC; simulation and programming.	Tear on back and arms.	1	1	1	1	1	This work has not been dangerous to the student or other. Work position can make tear on arms and back. Eyes can get problems with, after work on computer.

Likelihood, e.g.:

1. *Minimal*
2. *Low*
3. *High*
4. *Very high*

Consequence, e.g.:

1. *Relatively safe*
2. *Dangerous*
3. *Critical*
4. *Very critical*

Risk value (each one to be estimated separately):
Human = Likelihood x Human Consequence
Environmental = Likelihood x Environmental consequence
Financial/material = Likelihood x Consequence for Economy/materiel

Potential undesirable incident/strain

Identify possible incidents and conditions that may lead to situations that pose a hazard to people, the environment and any materiel/equipment involved.

Criteria for the assessment of likelihood and consequence in relation to fieldwork

Each activity is assessed according to a worst-case scenario. Likelihood and consequence are to be assessed separately for each potential undesirable incident. Before starting on the quantification, the participants should agree what they understand by the assessment criteria:

The likelihood of something going wrong is to be assessed according to the following criteria:

1 **Minimal**
Once every 10 years or less

2 **Low**
Once a year

3 **High**
Once a month

4 **Very high**
Once a week or more often

Human consequence is to be assessed according to the following criteria:

1 **Relatively safe**
Injury that does not involve absence from work; insignificant health risk

2 **Dangerous**
Injury that involves absence from work; may produce acute sickness

3 **Critical**
Permanent injury; may produce serious health damage/sickness

4 **Very critical**
Injury that may produce fatality/ies

Environmental consequences are assessed according to the following criteria:

1 **Relatively safe**
Insignificant impact on the environment

2 **Dangerous**
Possibility of undesirable long term effects; some cleanup is to be expected

3 **Critical**
Undesirable long term effects; cleanup to be expected

4 **Very critical**
Damaging to living organisms; irreversible impact on the environment; cleanup must be undertaken

The unit makes its own decision as to whether opting to fill in or not consequences for economy/materiel, for example if the unit is going to use particularly valuable equipment. It is up to the individual unit to choose the assessment criteria for this column.

Risk = Likelihood x Consequence

Please calculate the risk value for “Human”, “Environment” and, if chosen, “Economy/materiel”, separately. For activities with a risk value of 16 or 12, or a single value of 4, safety measures (designed to both reduce the likelihood and to limit the consequences) must be documented with descriptions of measures and allocation of responsibility.

About the column ”Comments/status, suggested preventative and corrective measures”:

Measures can impact on both likelihood and consequences. Prioritise measures that can prevent the incident from occurring; in other words, likelihood-reducing measures are to be prioritised above greater emergency preparedness, i.e. consequence-reducing measures.

NTNU HSE	HSE action plan	Prepared by	Number	Date
		The HSE section	HMSRV-12/24	01.12.2006
		Approved by	Page	Replaces
		The Rector	1 of 1	20.08.1999

Unit:Chemical Engineering

What	**Measure**	**Unit responsible**	**Priority**	**Cost**	**Current status**
Programming and simulation does not need HSE action plant					

Date: ______________________ Line manager: ____

NTNU	Hazardous activity identification process	Prepared by	Number	Date
		HSE section	HMSRV-26/01	01.12.2006
		Approved by	Page	Replaces
HSE		The Rector	1 out of 1	15.12.2003

Unit: Chemical Engineering **Date: 30.05.11**

Participants in the identification process (including their function):

Short description of the main activity/main process: Simulation and programming on computer.

Activity/process	**Responsible person**	**Laws, regulations etc.**	**Existing documentation**	**Existing safety measures**	**Comment**
Simulation and programming on computer	Sigurd Skogestad	-	-	-	Not a safety problem in this work.