ADVANCED MODELLING OF EMULSION TERPOLYMERISATION FOR ONLINE OPTIMISATION AND CONTROL

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B.Sc (Analytical Chemistry), M.Sc (Physical Chemistry)

This thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

In Process Systems Engineering
School of Chemical and Bio-Molecular Engineering

University of Sydney
Australia
2008
DECLARATION

I declare that the entire contents of this thesis are, to the best of my knowledge and belief, original, unless otherwise acknowledged in the text. I have not submitted this material, in whole or part, for another degree at this or any other institution.

Mourtada Hussein Srour

March 2008
ACKNOWLEDGMENT

Thanks God for Your mercy upon me by granting me the opportunity to experience such great postgraduate study at the School of Chemical and Biomolecular Engineering at Sydney University.

First of all I would like to thank the dearest persons to my heart in this world who have always looked after me, who are my mother and father.

Then I wish to thank my supervisor A/Prof. Vincent Gomes who dedicated a lot throughout my study, and who taught me much about a commitment, hardwork, knowledge, vision and friendship. I also would like to thank Prof. Jose Romagnoli for his continuous assistance and support. A special thanks to Dr. Ali Abbas who enrolled and guided me at the beginning of my research.

I also wish to thank all the members of the PSE group, Dr. Bassam Alhamad, Dr. Pablo Rolandi, Dr. Abd Halim Shah Maulud, Dr. Dawie Wang, Seyed Mustafa Nowee, Bhaharat Bhushan, Rob Willis, Rebecca Elgebrandt, Shahla Ghaffari, Mitra Ahmadi, Ronald Chew, Jose Martin Korath, Saleh Rawadieh and Ibrahim Altarawneh who all are my great friends and never will be forgotten.

The technical and administrative staff in the school have contributed towards the success of many students, especially Denis Trevaskis, Annette, Ellen, Javier, Regina, Katharyn and Jeffrey. The financial scholarship from the Australian Research Council is gratefully acknowledged. The School of Chemical and Biomolecular Engineering at Sydney University is gratefully appreciated for giving me the opportunity to prepare my thesis. I also would like to thank all of my relatives here in Australia especially my uncle Mouse Dakdouk and my aunt Zahra Dakdouk, her husband Ahmad El-Zien and her sons Ali and Mohammad for their fruitful support.

Finally, I would like to mention thanks to my brothers, sisters and my wife Rabab above all for their kind support.
TO whom will save humanity
TO whom will light darkness
TO the waited leader of humanity

AL-IMAM ALMEHDI
ABSTRACT

Polymer manufacturing is a major worldwide industry, attracting the attention of numerous industrial units and research institutes. Increasing demands on polymer quality, process safety and cost reduction are the main reasons for growing interest in the design and control of emulsion polymerisation. Emulsion polymerisation process implemented with free radical polymerisation has significant advantages over other processes, such as the production of polymer of higher molecular weights at high conversion rates, easier temperature control due to the low viscosity of the reaction media, high degree of selectivity and more friendly to environment due to the use of an aqueous medium. It allows for the production of particles with specially-tailored properties, including size, composition, morphology, and molecular weights. Introducing two or more different monomers to the polymerisation process (named multi-polymerisation) can lead to the synthesis of an almost unlimited number of new polymers types.

Emulsion polymers are products by process, meaning that the manner in which the polymerisation is carried out is perhaps more important than the raw materials in determining the form of the final product. This highlights the significance of the systematic approach in online process control which requires thorough understanding of the process phenomena as a prerequisite for development of a mathematical description of the process as the model. It is thus evident and based on research observations that process control for emulsion terpolymerisation is a particularly difficult task because of the lack of validated models and the lack of online measurements of most of polymer properties of interest. Therefore, a well validated model is crucial for optimising and controlling the emulsion terpolymerisation operations allowing for design of the polymer product properties.

In this study, a framework for process design and control of emulsion terpolymerisation reactors was developed. This framework consisted of three consecutive stages, dynamic modelling of the process, optimising the process for
finding the optimal operating strategies and final online controlling the obtained optimal trajectories through multivariable constrained model predictive control.

Within this framework, a comprehensive dynamic model was developed. Then a test case of emulsion terpolymerisation of styrene, methyl methacrylate and methyl acrylate was investigated on state of the art facilities for predicting, optimising and control end-use product properties including global and individual conversions, terpolymer composition, the average particle diameter and concentration, glass transition temperature, molecular weight distribution, the number- and weight-average molecular weights and particle size distribution. The resulting model was then exploited to understand emulsion terpolymerisation behavior and to undertake model-based optimization to readily develop optimal feeding recipes. The model equations include diffusion-controlled kinetics at high monomer conversions, where transition from a ‘zero-one’ to a ‘pseudo-bulk’ regime occurs. Transport equations are used to describe the system transients for batch and semi-batch processes. The particle evolution is described by population balance equations which comprise of a set of integro-partial differential and nonlinear algebraic equations. Backward finite difference approximation method is used to discretise the population equation and convert them from partial differential equations to ordinary differential equations. The model equations were solved using the advanced simulation environment of the gPROMS package.

The dynamic model was then used to determine optimal control policies for emulsion terpolymerisation in a semi-batch reactor using the multiobjective dynamic optimisation method. The approach used allows the implementation of constrained optimisation procedures for systems described by complex mathematical models describing the operation of emulsion terpolymerisation reactors. The control vector parameterisation approach was adopted in this work. Styrene monomer feed rate, MMA monomer feed rate, MA monomer feed rate, surfactant feed rate, initiator feed rate and the temperature of reactor were used as the manipulating variables to produce terpolymers of desired composition, molecular weight distribution (MWD) and particle size distribution (PSD). The particle size polydispersity index (PSPI), molecular weight polydispersity index (MWPI) and the overall terpolymer composition ratios were incorporated as the objective functions to optimise the PSD,
MWD and terpolymer composition, respectively. The optimised operational policies were successively validated with experiments via one stirred tank polymerisation reactor.

Due to the lack of online measurements of key process product attributes for emulsion terpolymerisation, an inferential calorimetric soft sensor was developed based on temperature measurements. The calorimetric soft sensor obtains online measurements of reactor temperature, jacket inlet and outlet temperatures helped estimate the rate of polymerisation. The model includes the mass and energy balance equations over the reactor and its peripherals. Energy balance equations include the heat of reaction, internal and external heat transfer effects, as well as external heat losses.

An online multivariable constrained model predictive control was formulated and implemented for online control of the emulsion terpolymerisation process. To achieve this implementation, a novel generic multilayer control architecture for real-time implementation of optimal control policies for particulate processes was developed. This strategy implements the dynamic model for the emulsion terpolymerisation as a real-time soft sensor which is incorporated within the implemented MPC. The methodology was successively validated using six case studies within the on-line control of terpolymerisation reactors. The cases were online controlled the composition of terpolymers, PSD and Mn with specific constraints for the operation conversion and particle average radius.

An advanced Supervisory Control Architecture named ROBAS was used in this work. It provides a completely automated architecture allowing for the real time advanced supervisory monitoring and control of complex systems. The real time control application strategy was developed within MATLAB, Simulink, gPROMS and Excel Microsoft softwares and implemented on line through ROBAS Architecture.

The manipulated variables are measured using on-line measurements connected to the DCS system through Honeywell. These measurements were sent to MATLAB and then to the dynamic model in gPROMS through an excel spread-sheet interface. Then the dynamic model used them to estimate the controlled variables of the MPC. The estimated values of the controlled variables obtained from the dynamic model, were
then sent to the Simulink and fed through the DCS system to the MPC developed in MATLAB. The MPC would then calculate optimal trajectories, which are then sent as set point signals through the DCS system to the regulatory controller.

The MPC formulation was found to be robust and handles disturbances to the process. The result showed that the online multivariable constrained MPC controller was able to control the desired composition and Mn as specified set points with great accuracy. The MPC algorithm succeeded under constrained conditions, in driving the PSD to the desired target. Although some offset was observed with a certain degree of model mismatch, the experimental results agreed well with predictions.
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FIGURE 5.3 Validation of optimisation for maximizing MWPI, (a) & (b) Variable optimal profiles, (c) MWPI, (d) MWD, (e) Conversion, (f) Particle Diameter (● experiment; ▬ 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FIGURE 6.7 Validation of online multivariable constrained MPC for terpolymer composition control with \( r_1 \) as a set points: (a) obtained optimal feed rate profile, (b) terpolymer composition, (c) Conversion, (d) Particle Diameter (● experiment; — simulation).………………………………………………………. 6.27

FIGURE 6.8 Validation of online multivariable constrained MPC for terpolymer composition control with \( r_2 \) as a set points: (a) obtained optimal feed rate profile, (b) terpolymer composition, (c) Conversion, (d) Particle Diameter (● experiment; — simulation).………………………………………………………………. 6.28

FIGURE 6.9 Validation of online MPC for terpolymer composition control with \( r_3 \) as a set points: (a) obtained optimal feed rate profile, (b) terpolymer composition, (c) Conversion, (d) Particle Diameter (● experiment; — simulation).………………………………………………………………. 6.28

FIGURE 6.10 Experimental PSPI using online MPC: a) Maximising PSPI (bimodal PSD); b) Minimising PSPI (mono-modal PSD).……… 6.31

FIGURE 6.11 Validation of online multivariable constrained MPC for maximising PSPI: (a) obtained optimal feed rate profile, (b) Particle Diameter, (c) PSD, (d) Conversion (● experiment; — Setpoint; — Sensor estimation).…………………………………………….. 6.32

FIGURE 6.12 Validation of online multivariable constrained MPC for minimising PSPI: (a) obtained optimal feed rate profile, (b) Particle Diameter, (c) PSD, (d) Conversion (● experiment; — Setpoint; — Sensor estimation).…………………………………………….. 6.33

FIGURE 6.13 Validation of online multivariable constrained MPC for minimising Mn: (a) & (b) obtained optimal feed rate profiles, (c) Mn, (d) Conversion, (e) Particle Diameter (● experiment; — Setpoint; — Sensor estimation).…………………………………………….. 6.35

FIGURE 6.14 Validation of online multivariable constrained MPC for maximising Mn: (a) obtained optimal feed rate profile, (b) Mn, (c) Conversion, (d) Particle Diameter (● experiment; — Setpoint; — Sensor estimation).…………………………………………….. 6.36
NOMENCLATURE

A  Heat transfer area (m$^2$)
$a_g$  Empirical constant for glass transition temperature.
$a_s$  Polymer particle area occupied by an adsorbed surfactant molecule, dm$^2$
$C_{sat}$  Saturated concentration of monomer $l$ in i phase, mol.L$^{-1}$
$C_p$  Concentration of monomers in polymer particle phase, mol.L$^{-1}$
$C_w$  Concentration of monomers in aqueous phase, mol.L$^{-1}$
$C_{sat}$  Saturated concentration of monomers in aqueous phase, mol.L$^{-1}$
$C_{d,i}$  Concentration of monomer $l$ in droplet phase, mol.L$^{-1}$
$C_{p,l}$  Concentration of monomer $l$ in the latex particles, mol.L$^{-1}$
$C_{Pi}$  Heat capacity of reactor content i (J/g·K)
$C_{w,l}$  Concentration of monomer $l$ in the water phase, mol.L$^{-1}$
$C_{micelle}$  Concentration of micelles, mol L$^{-1}$
$[\text{cmc}]$  Critical micelle concentration, mol L$^{-1}$
$D$  Reactor diameter (m)
$D_{mon,l}$  Diffusion coefficient of monomer $l$ in particle phase, dm$^2$
$D_{w,l}$  Diffusion coefficient of monomer $l$ in water phase, dm$^2$
$D_{rd,l}$  Diffusion coefficient arising from reaction-diffusion, dm$^2$
$d$  Impeller diameter (m)
$d_{p,l}$  Density of polymer $l$, kg L$^{-1}$
$d_{m,l}$  Density of monomer $l$, kg L$^{-1}$
$\Delta H_i$  Enthalpy of monomer i homopolymerisation (J/mol)
$[\text{E} \cdot \text{l}]$  Aqueous phase concentration of desorbed radicals, mol.L$^{-1}$
$e_e$  Entry efficiency coefficient
$f$  Efficiency dissociation constant
$F_{comp,l}$  Mole fraction of monomer $l$ in the polymer
$F_I$  Flow rate of initiator, mol.s$^{-1}$
$f_i$ Mole fraction of monomer $l$ in the system

$F_{m,l}$ Flow rate of monomer $l$, g.s$^{-1}$

$F_s$ Flow rate of surfactant, mol.s$^{-1}$

$F_w$ Flow rate of monomer, L.s$^{-1}$

$G$ The number of radius increments to be integrated

$h_t$ Transfer coefficient between the reaction mixture and the internal wall(W/m$^2$K)

$[I]$ Initiator concentration in the reactor, mol.L$^{-1}$

$[IM^*]$ Aqueous phase concentration of oligomeric radicals of degree ‘i’, mol.L$^{-1}$

$j_{cr}$ Critical degree of polymerisation for homogeneous nucleation

$K_s$ Stirrer constant

$K$ Rate of propagation volume growth per particle, L s$^{-1}$

$K_{i,j}$ Partition coefficient of monomer $l$ between i and j phases

$k_d$ Rate coefficient for initiator decomposition, s$^{-1}$

$k_{dm}$ Rate coefficient for desorption of monomeric radicals from particles, s$^{-1}$

$k_{dm,l}$ Rate coefficient for desorption of monomeric radicals $l$ from particles of radius $j$, s$^{-1}$

$k_{diff,l}$ Diffusion-controlled rate coefficient of monomeric radicals $l$, s$^{-1}$

$k_{e,l}$ Rate coefficient for entry of an oligomeric radical $l$ of degree ‘i’ into an existing particle of radius $j$, L.mol$^{-1}$.s$^{-1}$

$k_{e,j}$ Overall rate coefficient for entry of oligomeric radical of degree ‘i’ into an existing particle of radius $j$, L.mol$^{-1}$.s$^{-1}$

$k_{eE}$ Overall rate coefficient for re-entry of desorbed monomeric radicals $l$, L.mol$^{-1}$.s$^{-1}$

$k_{eE,l}$ Overall rate coefficient for re-entry of desorbed monomeric radicals $l$ into an existing particle of radius $j$, L.mol$^{-1}$.s$^{-1}$

$k_{e,micelle}$ Rate coefficient for entry of an oligomeric radical of degree ‘i’ into a micelle, L.mol$^{-1}$.s$^{-1}$

$K_i$ Volume growth rate coefficient for free monomeric radical $l$ existing in a particle, L.mol$^{-1}$.s$^{-1}$
$k_p$ General propagation rate coefficient in polymer particle, L.mol$^{-1}$.s$^{-1}$

$K_{po}$ Propagation rate coefficient at low conversion in polymer particle, L.mol$^{-1}$.s$^{-1}$

$k_{p,ij}$ Propagation rate coefficient of polymeric radical $i$ with monomer $j$, L.mol$^{-1}$.s$^{-1}$

$k_{p,eq}^{i}$ Aqueous phase propagation rate coefficient for oligomeric radicals of degree ‘i’, L.mol$^{-1}$.s$^{-1}$

$k_{p,aq}$ Overall aqueous phase propagation rate, L.mol$^{-1}$.s$^{-1}$

termination rate coefficient between oligomeric radicals of degree ‘$i$’ and ‘$j$’ in phase $l$, L.mol$^{-1}$.s$^{-1}$

$k_{t,ij}$ Termination rate coefficient between oligomeric radicals in particle phase at low conversion, L.mol$^{-1}$.s$^{-1}$

$k_{t,aq}$ Overall termination rate coefficient in the aqueous phase, L.mol$^{-1}$.s$^{-1}$

$k_{t,aq}^{i}$ Termination rate coefficient between oligomeric radicals of degree ‘$i$’ and ‘$j$’ in the aqueous phase, L.mol$^{-1}$.s$^{-1}$

$k_{tr}$ Rate coefficient for radical transfer to monomer, L.mol$^{-1}$.s$^{-1}$

$M$ Molecular weight of polymer chain, kg.mol$^{-1}$

$M_{avg}$ Average molecular weight of the different monomers, kg.mol$^{-1}$

$M_l$ Molecular weight of monomer $l$, kg.mol$^{-1}$

$M_n$ Number average molecular weight, kg.mol$^{-1}$

$M_w$ Weight average molecular weight of polymer, kg.mol$^{-1}$

$N$ Agitation speed (rev/s)

$N_A$ Avogadro’s constant, mol$^{-1}$

$N_t$ Total number of moles of monomer $l$ in the system, mol

$N_{fed,l}$ Total number of moles of monomer $l$ added to the system, mol

$N_t$ Total number of moles of all monomers in the system, mol

$N_{terp,l}$ Number of moles of monomer $l$ in the polymer, mol

$N_{p}$ Total number of polymer particles in the reactor, particles

$n_{agg}$ Micelle aggregation number, i.e. the average number of surfactant molecules in a micelle

$n(v)$ Molar concentration density of particles of unswollen volume $v$, mol.L$^{-1}$.dm$^{-1}$
\( n_0(v) \) Molar concentration density of particles of unswollen volume \( v \) containing no radicals, \( \text{Mol.L}^{-1}\text{.dm}^{-1} \)

\( n_i^m(v) \) Molar concentration density of particles of unswollen volume \( v \) containing monomeric radicals, \( \text{mol.L}^{-1}\text{.dm}^{-1} \)

\( n(G) \) Molar concentration density of particles of radius increments \( G \), \( \text{mol.L}^{-1}\text{.dm}^{-1} \)

\( n_u(G) \) Molar concentration density of particles of radius increments \( G \) containing no radicals, \( \text{mol.L}^{-1}\text{.dm}^{-1} \)

\( n_i^m(G) \) Molar concentration density of particles of radius increments \( G \) containing monomeric radicals, \( \text{mol.L}^{-1}\text{.dm}^{-1} \)

\( n_i^p(G) \) Molar concentration density of particles of radius increments \( G \), containing polymeric radicals, \( \text{mol.L}^{-1}\text{.dm}^{-1} \)

\( P(M) \) Instantaneous molecular weight distribution

\( \bar{P}(M) \) Cumulative molecular weight distribution

\( PSPI \) Particle size polydispersity index

\( Q_f \) Heat flux across the reactor wall (W)

\( Q_l \) Heat losses (W)

\( Q_r \) Heat-generation rate due to the chemical reaction (W)

\( Q_{st} \) Heating due to stirrer (W)

\( Q_{feed} \) Heat flow due to the reactor feed (W)

\( R_p \) Polymerisation reaction rate, \( \text{mol. L}^{-1}\text{.s}^{-1} \)

\( R_{i,l} \) Rate of polymerisation of monomer \( l \) in phase \( i \), \( \text{mol. L}^{-1}\text{.s}^{-1} \)

\( r_s \) Swollen radius of latex particle, dm

\( r_u \) Unswollen radius of latex particle, dm

\( [S] \) Concentration of added surfactant per unit volume of the aqueous phase, \( \text{mol L}^{-1} \)

\( [S_{ads}] \) Concentration of adsorbed surfactant on the polymer particles surface, \( \text{mol L}^{-1} \)

\( T \) Temperature of the reaction, K

\( T_{amb} \) Ambient temperature (°C)

\( T_r \) Reactor temperature (°C)

\( T_{j,out} \) Outlet jacket temperature (°C)
\[ T_{j,in} \] Inlet jacket temperature (°C)
\[ T_w \] Reactor wall temperature (°C)
\[ T_g \] Glass transition of polymer, K
\[ T_{g,l} \] Glass transition of polymer formed from monomer \( l \), K
\[ [f^*] \] Total oligomers concentration in the aqueous phase, mol.L\(^{-1}\)
\[ U \] Heat transfer coefficient (W/m\(^2\)K)
\[ V \] Total volume of polymerisation reaction, m\(^3\)
\[ V_d \] Total volume of monomer droplets in the system, dm\(^3\)
\[ V_p \] Total volume of polymer in the system, dm\(^3\)
\[ V_s \] Volume of swollen polymer particle, dm\(^3\)
\[ V_u \] Volume of unswollen polymer particle, dm\(^3\)
\[ V_w \] Volume of aqueous phase in the system, L
\[ V_{w,0} \] Volume of water in the system, L
\[ V_{w,m} \] Volume of dissolved monomers in water, L
\[ X \] Total instantaneous monomers weight conversion
\[ X_l \] Instantaneous molar conversion monomer \( l \)
\[ z \] Critical degree of polymerisation for entry

**Greek letters**

\( \rho \) Pseudo rate coefficient for all entry events (oligomeric radicals and exited radicals) into existing particles, \( s^{-1} \)
\( \rho_{init} \) Pseudo rate coefficient for entry of an oligomeric radical into an existing particle, \( s^{-1} \)
\( \alpha \) Coefficient for heat losses (W/°C\(^d\))
\( \beta \) Power coefficient for heat losses
\( \rho_l \) Density of latex (Kg/m\(^3\))
\( \rho_m \) Density of monomer (Kg/m\(^3\))
\( \rho_p \) Density of polymer (Kg/m\(^3\))
\( \rho_w \) Density of water (Kg/m\(^3\))