1-1-2007

Modeling and optimization of ethylene copolymerization in high pressure reactor using difunctional initiators

Pegah Khazraei Karimi Fard
Ryerson University

Follow this and additional works at: <http://digitalcommons.ryerson.ca/dissertations>

Part of the [Chemical Engineering Commons](#)

Recommended Citation

Fard, Pegah Khazraei Karimi, "Modeling and optimization of ethylene copolymerization in high pressure reactor using difunctional initiators" (2007). *Theses and dissertations*. Paper 242.

This Thesis is brought to you for free and open access by Digital Commons @ Ryerson. It has been accepted for inclusion in Theses and dissertations by an authorized administrator of Digital Commons @ Ryerson. For more information, please contact bcameron@ryerson.ca.

**MODELING AND OPTIMIZATION OF ETHYLENE
COPOLYMERIZATION IN HIGH PRESSURE REACTOR
USING DIFUNCTIONAL INITIATORS**

TP
248
E73
F37
2007

By

Pegah Khazraei Karimi Fard

Bachelor of Chemical Engineering, Tehran University, Iran, 1997

Master of Science, Sharif University of Technology, Iran, 2003

A thesis

presented to Ryerson University

in partial fulfillment of the
requirements for the degree of

Master of Applied Science

In the Program of

Chemical Engineering

Toronto, Ontario, Canada, 2007

© Pegah Khazraei Karimi Fard 2007

UMI Number: EC53647

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI Microform EC53647
Copyright 2009 by ProQuest LLC
All rights reserved. This microform edition is protected against
unauthorized copying under Title 17, United States Code.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

Author's Declaration

I hereby declare that I am the sole author of this thesis. I authorize Ryerson University to lend this thesis to other institutions or individuals for the purpose of scholarly research.

Pegah Khazraei

I further authorize Ryerson University to reproduce this thesis by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research.

Pegah Khazraei

Borrower's Page

Ryerson University requires the signature of all persons using or photocopying this thesis. Please sign below and give address and date.

MODELING AND OPTIMIZATION OF ETHYLENE COPOLYMERIZATION IN HIGH PRESSURE REACTOR USING DIFUNCTIONAL INITIATORS

Pegah Khazraei Karimi Fard

Master of Applied Science

Department of Chemical Engineering

Ryerson University

Abstract

Free radical (co-)polymerization of low-density polyethylene (LDPE) is carried out commonly in high pressure autoclave or tubular reactors. The severe thermodynamic conditions of the process hinder ethylene from going to full conversion. One remedy to improve the monomer conversion is to investigate the effectiveness of initiators, such as difunctional organic peroxides. In the present work, a kinetic model based on a postulated reaction mechanism for free radical ethylene (co-)polymerization initiated by difunctional initiators is applied to analyze the dynamic behavior of a continuous LDPE isothermal autoclave reactor and a non-isothermal tubular reactor. The model describes the rates of initiation, propagation and the population balance equations. It predicts variations of the initiator and monomer concentrations and reaction temperature as well as molecular weight distribution, long/short chain branching frequencies and the composition distribution of reactive macromolecular species. Variations of the pressure, velocity and transport/physical properties of the reacting mixture were accounted for in the tubular reactor. Model predictions are compared to experimental data collected from literatures for one monofunctional (dioctanoyl) and two difunctional initiators namely, (2,2-bis(tert-butylperoxy)-butane and 2,5-dimethyl hexane-2-t-butylperoxy-5-perpivalate). In comparison with dioctanoyl peroxide, polymerization with difunctional initiators requires lesser amount of initiators and gives higher ethylene conversion in shorter time.

The modeling of LDPE with difunctional initiators was then extended to ethylene copolymerization with vinyl acetate and butyl acrylate. The model helps to determine the influence of reactivity ratio on the end-use product properties. Details of modeling a multiple feed LDPE tubular reactor are included for both homo- and co-polymerization reactions. The effect of monomer and initiator injections on the productivity and (co-)polymer rheology and composition are investigated as well.

Finally, an optimization method was applied to determine the optimal values of control variables via maximization of an objective function expressed in terms of monomer conversion, number average molecular weight, polydispersity and final desired composition of copolymer product. The results show that we can obtain a polymer with desired characteristics by proper manipulation of the control variables.

Keywords: Ethylene (co)-polymerization, Di-functional peroxides, Modeling, Optimization.

Acknowledgement

I wish to express my deepest gratitude to my supervisor Dr. Dhib for his invaluable guidance and wealth of knowledge imparted to me during the development of this work and most for his patience and the support and extensive help he offered me to pass all the problems.

I wish to extend my sincere appreciation to the committee members, Drs. Philip Chan, Farhad Ein Mozaffari and Yasser Dahmane, for their valuable suggestions and comments.

My special thanks to my husband, Behzad for his constant help and encouragement in every aspect during my study at Ryerson University.

The financial assistance provided by NSERC and School of graduate studies at Ryerson University is also gratefully acknowledged.

Dedications

I wish to dedicate this thesis to my parents Rezvan and Ali and also to my beautiful baby girl, Elnaz.

Table of Contents

	Page
AUTHOR'S DECLARATION	ii
BORROWER'S PAGE	iii
ABSTRACT.....	iv
ACKNOWLEDGEMENT	vi
DEDICATIONS	vii
LIST OF FIGURES	xi
LIST OF TABLES	xvi
NOMENCLATURE	xvii
 CHAPTER 1 INTRODUCTION	 1
CHAPTER 2 LITERATURE REVIEW	4
2.1 LDPE reactor modeling	4
2.2 Difunctional initiators	8
 CHAPTER 3 HOMO-POLYMERIZATION OF ETHYLENE IN AUTOCLAVE AND TUBULAR REACTORS USING DIFUNCTIONAL INITIATORS.....	 11
3.1 Reaction mechanism.....	11
3.2 Kinetic rate constants.....	14
3.3 Dynamic modeling of an isothermal autoclave CSTR reactor.....	16
3.3.1 Reactor model.....	16
3.3.2 Population balance moments.....	17
3.3.3 Moments of live polymer balance	18
3.3.4 Moments of dead polymer balances	19
3.3.5 Molecular properties balances.....	21
3.3.6 Calculation of molecular weight distribution.....	23
3.4 Modeling of tubular LDPE reactor.....	23
3.4.1 Live polymer moment equations	26
3.4.2 Polymer model.....	26

3.4.3 Molecular properties balances	27
3.4.4 Physical and transport properties	29
3.5 Multiple feed tubular reactor.....	32
3.5.1 Mixing point equations	33
3.6 Results and discussion	35
3.6.1 Model validation with CSTR data	36
3.6.2 Simulation of a LDPE isothermal autoclave reactor	38
3.6.3 Simulation of tubular reactor.....	45
3.6.2.3 Effect of multiple feed on polymer properties in tubular reactor	56
CHAPTER 4 CO-POLYMERIZATION OF ETHYLENE IN AUTOCLAVE AND TUBULAR REACTORS USING DIFUNCTIONAL INITIATORS	64
4.1 Pseudo-kinetic rate constant approach.....	66
4.2 Polymer reactor model	71
4.2.1 Ethylene copolymerization model in an isothermal autoclave reactor	71
4.2.2 Modeling copolymerization reaction in tubular reactor.....	74
4.2.3 Molecular properties for copolymerization.....	78
4.3 Simulation of ethylene copolymerization in tubular reactor	79
4.3.1 Effect of feed composition on reactor performance and product quality	79
CHAPTER 5 OPTIMIZATION OF LDPE REACTORS	93
5.1 Optimal control objective and decision variables	93
5.2 Tubular reactor optimization	95
5.2.1 Ethylene homopolymerization optimization	96
5.2.2 Ethylene copolymerization optimization	104
CHAPTER 6 Conclusions and Recommendations.....	109
6.1 Conclusions.....	109
6.2 Recommendations	110
REFERENCES.....	111
APPENDIX A. Organic Peroxides.....	120
APPENDIX B Initiators efficiency	122

APPENDIX C Reactions with internal radical centers.....	123
--	------------

List of Figures

<u>Figure 3.1:</u> Tubular reactor with three zones.....	33
<u>Figure 3.2:</u> Schematic description of mixing point.....	33
<u>Figure 3.3:</u> Prediction and data conversion versus temperature for ethylene bulk polymerization using dioctanoyl with initial concentration of 40 ppm P=1700 bar and $\theta_r = 65$ sec	39
<u>Figure 3.4:</u> Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,2-bis(tert-butylperoxy)butane with initial concentration of 20 mol ppm P=1700 bar and $\theta_r = 40$ sec	39
<u>Figure 3.5:</u> Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,2-bis(tert-butylperoxy)butane with initial concentration of 10 mol ppm P=1700 bar and $\theta_r = 40$ sec	40
<u>Figure 3.6:</u> Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate with initial concentration of 5 mol ppm P=1700 bar and $\theta_r = 60$ sec	40
<u>Figure 3.7</u> Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate with initial concentration of 10 mol ppm P=1700 bar and $\theta_r = 60$ sec	41
<u>Figure 3.8:</u> Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate with initial concentration of 25 mol ppm P=1700 bar and $\theta_r = 60$ sec	41
<u>Figure 3.9:</u> Average molecular weight predictions and data versus temperature for ethylene bulk polymerization. For initiators 2,2-bis(tert-butylperoxy)-butane (BU) and 2,5-dimethyl hexane -2-t-butylperoxy-5-perpivalate (DHBPPI) each with [I]=20 mol ppm, P=1700 bar and $\theta_r = 60$ sec	42
<u>Figure 3.10:</u> Predictions of polydispersity index of LDPE versus temperature. For dioctanoyl [I]=40 ppm, 2,2-bis(tert-butylperoxy)-butane (BU) and 2,5-dimethyl hexane -2-t-butylperoxy-5-perpivalate (DHBPPI) each with [I] =20 ppm.	42

<u>Figure 3.11</u> : Prediction of conversion versus time and temperatures for dioctanoyl with initial concentration of 40 mol ppm, P=1700 bar, $\theta_r = 65$ sec	43
<u>Figure 3.12</u> : Prediction of conversion versus time and temperatures for 2,2-bis(tert-butylperoxy)-butane with initial concentration of 10 mol ppm, P=1700 bar, $\theta_r = 40$ sec	43
<u>Figure 3.13</u> : Prediction of conversion versus time for different temperatures for 2,5-dimethyl hexane -2-t-butylperoxy-5-perpivalate with initial concentration of 10 mol ppm, P=1700 bar, $\theta_r = 60$ sec	44
<u>Figure 3.14</u> : Prediction of molecular weight distribution for Ethylene bulk polymerization using dioctanoyl, 2,2-bis(tert-butylperoxy)-butane and 2,5-dimethyl hexane -2-t-butylperoxy-5-perpivalate, with initial concentrations [I]= 20 ppm, P=1700 bar, T=230°C and $\theta_r = 60$ sec	44
<u>Figure 3.15</u> : Ethylene conversion profiles for different initiators at constant temperature 160 °C.	47
<u>Figure 3.16</u> : Initiator conversion profiles at constant temperature 160°C.	47
<u>Figure 3.17</u> : Average molecular weights at constant temperature 160°C.	48
<u>Figure 3.18</u> : Ethylene conversion profiles at constant temperature 270°C.	48
<u>Figure 3.19</u> : Initiators conversion profiles at constant temperature 270°C.	49
<u>Figure 3.20</u> : Average molecular weights at constant temperature 270°C.	49
<u>Figure 3.21</u> : Comparison of number- and weight- average molecular weights along the tubular reactor for different initiators at constant temperature 230°C.	50
<u>Figure 3.22</u> : Temperature profiles of different initiators.	52
<u>Figure 3.23</u> : Conversion profiles of different initiators.	52
<u>Figure 3.24</u> : Comparison of polydispersity along the tubular reactor for different initiators.	53
<u>Figure 3.25</u> : Comparison of number- and weight- average molecular weights a) versus reactor length b) versus conversion.	54
<u>Figure 3.26</u> : Prediction of long chain branching frequency for different initiators.	54
<u>Figure 3.27</u> : Prediction of short chain branching frequency for different initiators.	55
<u>Figure 3.28</u> : Prediction of vinylene group frequency for different initiators.	55

<u>Figure 3.29:</u> Prediction of vinylidene group frequency for different initiators.	56
<u>Figure 3.30:</u> Monomer mass flow rate for a) monomer and initiator injections at $z=0.3$ and $z=0.67$, b) no injection and c) initiator injection at two points at $z=0.3$ and $z=0.67$. ..	58
<u>Figure 3.31:</u> Initiator molar flow rate for a) monomer and initiator injections at $z=0.3$ and $z=0.67$, b) no injection and c) initiator injection at two points at $z=0.3$ and $z=0.67$	59
<u>Figure 3.32:</u> Predicted temperature profile.....	59
<u>Figure 3.33:</u> Predicted ethylene conversion	60
<u>Figure 3.34:</u> Prediction of initiator concentration.....	60
<u>Figure 3.35:</u> Prediction of initiator conversion.....	61
<u>Figure 3.36:</u> Predicted number and weight average molecular weights a) versus reactor length b) versus conversion.	62
<u>Figure 3.37:</u> Predicted polydispersity.....	62
<u>Figure 3.38:</u> Predicted long chain branching frequency.....	63
<u>Figure 3.39:</u> Reynolds number.....	63
<u>Figure 4.1:</u> Prediction of temperature Profile for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	82
<u>Figure 4.2:</u> Prediction of polymerization heat for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	83
<u>Figure 4.3:</u> Prediction of conversion for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	84
<u>Figure 4.4:</u> Prediction of average molecular weights for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	85
<u>Figure 4.5:</u> Prediction of rate of transfer to polymer for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	86
<u>Figure 4.6:</u> Prediction of rate of transfer to monomer for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	87
<u>Figure 4.7:</u> Prediction of rate of termination for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	88
<u>Figure 4.8:</u> Prediction of long chain branching for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	89

<u>Figure 4.9:</u> Prediction of short chain branching for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	90
<u>Figure 4.10:</u> Prediction of copolymer composition for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.	91
<u>Figure 4.11:</u> Ethylene-vinyl acetate accumulated copolymer compositions for injection of vinyl acetate	92
<u>Figure 4.12:</u> Ethylene-butyl acrylate accumulated copolymer compositions for injection of ethylene.	92
<u>Figure 5.1:</u> Base and optimal temperature profiles using dioctanoyl peroxide to maximize conversion.	97
<u>Figure 5.2:</u> Effect of optimal policies on maximizing conversion using dioctanoyl peroxide.	98
<u>Figure 5.3:</u> Base and optimal temperature profiles using 2,2-bis(tert-butylperoxy)-butane to maximize conversion.	99
<u>Figure 5.4:</u> Effect of optimal policies on maximizing conversion using 2,2-bis(tert-butylperoxy)-butane.	99
<u>Figure 5.5:</u> Base and optimal temperature profiles using 2,5-dimethylhexane-2-tert-butylperoxy-5-perpivalate to maximize conversion.	100
<u>Figure 5.6:</u> Effect of optimal policies on maximizing conversion using 2,5-dimethylhexane-2-tert-butylperoxy-5-perpivalate.	101
<u>Figure 5.7:</u> Base and optimal temperature profiles using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{M}_{nd} = 21900$	102
<u>Figure 5.8:</u> Effect of optimal policies on maximizing conversion using 2,2-bis(tert-butylperoxy)-butane with $\bar{M}_{nd} = 21900$	103
<u>Figure 5.9:</u> Effect of optimal policies on average molecular weight using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{M}_{nd} = 21900$	103
<u>Figure 5.10:</u> Base and optimal temperature profiles for ethylene/butyl acrylate copolymerization using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{BuA,d} = 12(\text{wt}\%)$	105

<u>Figure 5.11</u> : Effect of optimal policies on maximizing conversion for ethylene/butyl acrylate copolymerization using 2,2-bis(tert-butylperoxy)-butane with $\bar{F}_{BuA,d} = 12(\text{wt}\%)$	105
<u>Figure 5.12</u> : Effect of optimal policies on copolymer composition for ethylene/butyl acrylate copolymerization using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{BuA,d} = 12(\text{wt}\%)$	106
<u>Figure 5.13</u> : Base and optimal temperature profiles for ethylene/vinyl acetate copolymerization using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{VAc,d} = 12(\text{wt}\%)$	107
<u>Figure 5.14</u> : Effect of optimal policies on maximizing conversion for ethylene/vinyl acetate copolymerization using 2,2-bis(tert-butylperoxy)-butane with $\bar{F}_{VAc,d} = 12(\text{wt}\%)$	108
<u>Figure 5.15</u> : Effect of optimal policies on maximizing conversion for ethylene/vinyl acetate copolymerization using 2,2-bis(tert-butylperoxy)-butane with $\bar{F}_{VAc,d} = 12(\text{wt}\%)$	108

List of Tables

<u>Table 3.1:</u> Macromolecular Species	14
<u>Table 3.2:</u> Reaction rate constants in ethylene polymerization	15
<u>Table 3.3:</u> Decomposition rate constants of peroxide initiators	16
<u>Table 3.4:</u> Physical and transport properties	29
<u>Table 3.5:</u> LDPE autoclave reactor operating conditions.....	36
<u>Table 3.6:</u> Design features and operating conditions of LDPE tubular reactor.....	45
<u>Table 3.7:</u> Optimal operating conditions for LDPE tubular reactor	51
<u>Table 3.8:</u> Operating conditions for multiple feed tubular reactor	57
<u>Table 4.1:</u> Apparent rate constants for free-radical copolymerization.....	68
<u>Table 4.2:</u> Kinetic rate constants for vinyl acetate.....	70
<u>Table 4.3:</u> Kinetic rate constants for buthyl acrylate	71
<u>Table 4.4:</u> Physical and thermodynamic properties of vinyl acetate	75
<u>Table 4.5:</u> Physical and thermodynamic properties of butyl acrylate.....	75
<u>Table 5.1:</u> Reactor performance at optimal operating conditions for Dioctanoyl to maximize conversion.....	97
<u>Table 5.2:</u> Reactor performance at optimal operating conditions for 2,2-bis(tert-butylperoxy)-butane to maximize conversion.	98
<u>Table 5.3:</u> Reactor performance at optimal operating conditions for 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate to maximize conversion.	100
<u>Table 5.4:</u> Reactor performance at optimal operating conditions for 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{M}_{nd} = 21900$	102
<u>Table 5.5:</u> Reactor performance at optimal operating conditions for ethylene/butyl acrylate using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{BuA,d} = 12(\text{wt}\%)$	104
<u>Table 5.6:</u> Reactor performance at optimal operating conditions for ethylene/vinyl acetate using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{VAc,d} = 12(\text{wt}\%)$..	107

Nomenclature

A	frequency factor, s^{-1} or $L/mol\ s$
A	surface area ($\pi D_i/4$), cm^2
$C_j (j : m, I, S)$	concentration of monomer, initiators and solvent , mol/L
C_{LCB}	long chain branching concentration, mol/L
C_P	heat capacity , $cal/g.K$
C_{Pi}	heat capacity pure monomer, $cal/g.K$
C_{SCB}	short chain branching concentration, mol/L
C_{VNL}	vinyl group concentration, mol/L
C_{VND}	vinyledene group concentration, mol/L
D_i	inside diameter of reactor, cm
D_o	outer diameter of the reactor, cm
E	activation energy, cal/mol
E_v	activation energy for viscous flow, $kcal/kmol$
$F_j (j=M, I, S)$	molar flow rate of monomer, initiators and solvent , mol/ s
f	fanning friction factor
f_1	efficiency of original initiator
f_2	efficiency of initiator with undecomposed peroxide
h_i	inside (the reactor) film heat-transfer coefficient, cal/cm^2secK
h_w	wall (reactor) heat-transfer coefficient, cal/cm^2secK
$[I]$	initiator concentration, mol/L
k	thermal conductivity of the reaction mixture, $cal/cm.s.K$
k_b	rate constant for backbiting, s^{-1}
k_β	rate constant for β – scission, s^{-1}
k_d	decomposition rate constant of monofunctional peroxide, s^{-1}
k_{d1}	decomposition rate constant of original difunctional peroxide, s^{-1}
k_{d2}	decomposition rate constant of peroxide with undecomposed radical, s^{-1}
k_p	rate constant of propagation, $L/ mol\ s$
k_{tc}	rate constant of termination by combination, $L/ mol\ s$

k_{td}	rate constant of termination by disproportionation, L/ mol s
k_{th}	rate constant of thermal initiation, L/ mol s
k_{tfm}	rate constant of transfer to monomer, L/ mol s
k_{tp}	rate constant of transfer to polymer, L/ mol s
k_{ts}	rate constant of transfer to solvent, L/mol
L	reactor length, m
$[M]$	monomer concentration, mol/L
$[M]_f$	monomer concentration after mixing point
$[M]_o$	monomer concentration before mixing point
$\bar{M}_i$	molar flow rate of monomer injected to reactor, mol/s
$\bar{M}_w$	weight average molecular weight, g/mol
$\bar{M}_n$	number average molecular weight, g/mol
Nu	Nusselt number
P	pressure, bar
P_c	critical pressure, MPa
P_r	Prandtl number
$[P_r]$	dead polymer concentration, mol/ L
$[\tilde{P}_r]$	dead polymer concentration with one undecomposed peroxide, mol/ L
$[\tilde{\tilde{P}}_r]$	dead polymer concentration with two undecomposed peroxide, mol/ L
Re	Reynolds number
R_I	rate of initiation without undecomposed peroxide
$\tilde{R}_I$	rate of initiation with undecomposed peroxide
R_p	rate of polymerization, mol/L s
$R_{in}^\bullet$	primary initiator radical fragment
$\tilde{R}_{in}^\bullet$	initiator radical fragment with one undecomposed peroxide
$R_r^\bullet$	radical of chain length r
$\tilde{R}_r^\bullet$	macroradical of chain length r , with one undecomposed peroxide
T	reaction temperature, K

T_c	critical temperature, K
T_r	reduced temperature
u	velocity, cm/s
U	overall heat transfer coefficient, cal/cm ² secK
$V_{M,E}$	specific volume of monomer, cm ³ /g
$V_{P,E}$	specific volume of polymer, cm ³ /g
w	mass fraction
$y_i (i = M, I, S)$	monomer, initiator and solvent conversion

Subscripts

f	reaction mixture property after mixing point
I	initiator
M	monomer
P	polymer
r	chain length
S	solvent
o	property of the reaction mixture before mixing point
0	initial condition, subscript for property at inlet to each section of tubular reactor

Greek Letters

Δv	activation volume, cm ³ /mol
$(-\Delta H_R)$	heat of reaction, cal/mol
λ_i	moments of live polymer radicals ($i = 0, 1, 2$)
$\tilde{\lambda}_i$	moments of live polymer radicals with one undecomposed peroxide ($i = 0, 1, 2$)
λ_{tot}	total concentration of live polymer radicals, mol/ L
μ_i	moments of P ($i = 0, 1, 2, 3$)

$\tilde{\mu}_i$	moments of $\tilde{P}$ ($i= 0, 1, 2,3$)
$\tilde{\tilde{\mu}}_i$	moments of $\tilde{\tilde{P}}$ ($i= 0, 1, 2$)
ρ	density , g/cm ³
ρ_r	reduced density
η	dense gas viscosity of the monomer, Pa.s
η^0	low pressure monomer viscosity, Pa.s
ξ	defined in Table 3.4, (Pa.s) ⁻¹

Chapter 1 Introduction

Low density polyethylene (LDPE) is one of the most important polymers used in the manufacture of a wide range of engineering and commodity plastics. The material appearance varies from translucent to opaque, from rigid or virtually unbreakable to flexible. LDPE is chemically not reactive and therefore, it is adaptable to almost all plastic fabrications. It is widely used for manufacturing various containers, tubing, computer components, car components and so forth. LDPE is commercially produced in a free radical ethylene polymerization which can be carried out in either tubular or autoclave reactors at high pressures (1000-3500 atm) and temperatures (150-300°C) in the presence of small amounts of chemical initiators (i.e. peroxides, azo compounds or oxygen). The severe thermodynamic condition of the process operation limits the process to be highly economically competitive since ethylene conversion remains low. As a result, improving the process performance has been a major concern in academia and industry.

Regarding the valuable industrial importance of the process, a number of academicians and industrialists incessantly attempted to establish a unified tangible understanding of ethylene polymerization in high-pressure reactors over the last few decades for both autoclave and tubular reactors (Goto et al., 1981, Gloor and Hamielec, 1993, Brandolin et al., 1988; Baltsas, Papadopoulos and Kiparissides, 1998). The efforts and interests in the studies in the open literature were propelled forward by the industrial and commercial importance of LDPE for the benefits of economical growth in contemporary society. However, the setback of obtaining only limited low conversion of ethylene in high-pressure polymerization has persistently been an unpleasant and discouraging reality in spite of many worthy attempts to enhance the conversion upon recycling the product and applying optimization schemes. Extensive studies on the kinetics of polymerization and modeling of the process were done. One of the most crucial problems encountered in operating a polyethylene reactor is to select the optimum operating conditions that maximize the reactor productivity at the desired product quality. Optimization schemes to determine optimal operating conditions were attempted in order to overcome the challenge of limited conversion and to maximize the reactor productivity with desired

product quality. Besides, the molecular structure and molecular weight distribution (MWD) of the polymer chains affect greatly the basic polymer properties like melt index, impact strength and rigidity, which are notably determining factors in shaping the quality of the end-product. Significant improvements came into light, but more research advancement is still needed.

Another route of enhancing ethylene conversion in this polymerization process is to examine the effectiveness of multifunctional initiators or difunctional peroxides, in particular. Multifunctional initiators can be used to increase the productivity of free radical polymerizations. The main characteristic of difunctional initiators is their sequential decomposition kinetics that generates high rates of polymerization while producing polymer of similar or higher molecular weights compared to monofunctional initiators. High molecular weights are beneficial to specific application such as extrusion coating. Furthermore, using difunctional initiators, reaction time could be reduced because of higher rate of polymerization. Another advantage of difunctional initiators is their ability to introduce branching into the final polymer product. When three or more labile groups are contained within a single molecule, the resulting polymer chain will have a structure resembling a star. The introduction of branching is an advantage for the polymer processing, especially in polymer stretching operations, to improve the melt strength.

Selection of the right peroxide to produce specific polymer grades at high rates of conversion is economically of great importance because peroxides are quite expensive and wastage is not affordable. With the exception of the experimental work of Luft et al. (1985a, b; 1988) and the theoretical study by Dhib and Al-Nidawy (2002), there is practically no study on the use of difunctional initiators in high pressure polyethylene process. However, a lot of work has been done using multifunctional peroxides for the production of low temperature polymers like polystyrene (Choi et al. 1987, 1988; Villalobos et al., 1991).

The motivation behind this work is propelled by the limited research on the use of multifunctional initiators in polyethylene production and the potential advantages that they may offer to improve the LDPE process. This main objective of study conducted in this thesis is to develop a comprehensive mathematical model which facilitates

determination the most favorable operating conditions of a tubular reactor for polymerizing ethylene and with one of its co-monomers such as vinyl acetate and butyl acrylate using difunctional peroxides. A number of simulation scenarios have been conducted.

In Chapter 2, a literature review of free radical polymerization of ethylene is presented. The review includes studies on modeling and optimization of LDPE processes in autoclave and tubular reactors, and also the work done on polyethylene production with difunctional initiators.

Chapter 3 consists of two sections. The first section deals with modeling and simulation of an unsteady state isothermal high-pressure autoclave reactor. The model is tested against experimental data collected from literature. A steady-state model is developed and discussed for LDPE process initiated with difunctional initiators in a tubular reactor. Multiple injections of monomer, initiator and solvent were included in the study. The effect of initiator type (di- or mono-functional) on productivity and molecular properties was investigated. Also, the influence of splitting the feed on the process performance was examined.

Since the synthesis of ethylene copolymers is of significant economical importance, a kinetic mechanism is proposed for ethylene/vinyl acetate and ethylene/butyl acrylate copolymerization using difunctional initiators and a related kinetic model is developed and thoroughly discussed in Chapter 4. The effects of multiple monomer feed on polymer composition were also investigated.

Chapter 5 examines optimization policies for homo- and co-polymerization in LDPE tubular reactors.

Chapter 6 summarizes the most important concluding remarks and proposes recommendations for future studies.

Chapter 2 Literature review

2.1 LDPE reactor modeling

For the polymerization of ethylene in high-pressure reactors, a variety of initiators can be used, depending on the type and structure of the desired polymer product. A number of interesting studies are reported in the literature on the modeling and optimization of LDPE reactors. Agrawal and Han (1975) studied various operating parameters affecting the performance of the reactor. They incorporated axial mixing to simulate the effect of pressure pulsing. However, Chen et al. (1976) showed that axial mixing can be neglected due to high Peclet number in a turbulent regime. Donati et al. (1982) accounted for the pulse valve effects using an average flow rate along the reactor and calculating only the pressure drop due to friction for an incompressible fluid. The most interesting observation that can be made from a survey of these modeling studies is the significant discrepancies in the values of the rate constants. These have been alluded to by Gupta et al. (1985).

Zabinsky et al. (1992), studied ethylene-vinyl acetate copolymerization in high-pressure tubular reactors using the pseudo-kinetic rate constants method. They proposed a kinetic mechanism based on terminal model theory including oxygen initiation and inhibition reactions, transfer to monomer, polymer and chain transfer agent, β -scission and terminal double-bond reactions and explosive decomposition of monomer and polymer at high temperatures. The model predicted the copolymerization rate and copolymer properties, including copolymer composition, molecular weight, branching frequencies, melt flow index and polymer density. The study included the modeling of a multizone high-pressure tubular reactor allowing for multiple feed points and multiple initiators. Also, the effect of the pulse valve and the product was incorporated. An instantaneous pressure drop was assumed, followed by a linear recovering of the pressure after each pulse. The model parameters were fitted to industrial data and comparison between the model predictions and industrial data was made. However, a substantial part of the rate constants in their study was adjusted.

In a review article by Kiparissides and Verros (1993a), the modeling of high-pressure ethylene (co)polymerization in tubular and autoclave reactors was discussed in detail. The simulation results for LDPE in both types of reactors for different operational conditions were presented and the effects of initiator concentration, inlet pressure, chain transfer concentration and wall fouling on the polymer quality and reactor operation was also illustrated. The paper also discussed variations of physical, thermodynamic and transport properties of ethylene and reaction mixture with temperature, pressure and composition were also discussed in this paper. Brandolin et al. (1996) simulated an industrial LDPE tubular reactor and calculated the kinetic parameters using the temperature profiles and the molecular properties of the product. Multiple injection of monomer, mixtures of initiators and chain transfer agents were considered together and their resulting simulation program was able to iterate in jacket temperature, jacket pressure and pressure drop due to pulse valve effects until convergence was achieved. Heat transfer coefficients were estimated from plant data, through appropriate energy balances giving careful consideration to the reactor geometry and the heat losses from non-insulated areas. Details on industrial data were not released.

Ham and Rhee (1996) developed a two-compartment four-cell model for an adiabatic small diameter type autoclave reactor for free radical polymerization of low density polyethylene (LDPE). They predicted the reactor performance in term of the monomer conversion and the reaction temperature and also the properties of the polymer product characterized by the average molecular weight and the polydispersity. The predictions were in good agreement with plant data and the properties of the polymer product were estimated within reasonable ranges of actual values. The temperature distribution was selected as the central parameter to control the properties of the polymer product in each compartment. They applied an adaptive controller to a highly nonlinear model representing the LDPE autoclave reactor. The adaptive pole-placement controllers were used during the start-up period, and a PID controller and a pole-placement controller were employed during steady state operation. In this case, the manipulated variables were the initiator feed rate to each compartment whereas the controlled variables were the exit temperature of each compartment. They concluded that as the reaction temperature changes very rapidly during the course of determining the control parameters due to the

fast initiator decomposition, the key to the adaptability of the control algorithm rests within the performance of the parameter estimator. Sarmoria and Brandolin (2000) incorporated mass balances of monomer, radical and polymer species to a mixing model for high pressure autoclave reactor for ethylene and ethylene/vinyl acetate polymerization. Ghiass and Hutchinson (2003) formulated a well-mixed kinetic model to study the steady state high pressure free- radical homo- and copolymerization of ethylene and vinyl- acetate in an industrial multi-feed, multi-zone autoclave reactor system. The multi-zone system was modeled as a simple set of well-mixed tank reactors in series. The effects of zone temperature, feed temperature and initiator decomposition kinetics on the steady state reactor performance and polymer properties were simulated and compared with industrial data. Ghiass and Hutchinson (2004) extended the model to a more complex compartment representation model to describe the imperfect mixing effects in an industrial multi-feed, multi- zone autoclave reactor at steady state operation conditions. In a more recent study, Kiparissides et al. (2005) developed a mathematical model for free-radical copolymerization of ethylene with various comonomers including ethyl acrylate, methyl acrylate and vinyl acetate in high-pressure tubular reactors. Their postulated model was in terms of leading moments of the bivariate number chain-length distributions of live and dead copolymer chains. They examined the model validity by tuning it online to real-time plant data and demonstrated the predictive capabilities of the model by direct comparison with industrial experimental data on the reactor temperature profile and pressure, the overall monomer conversion, and the final molecular and compositional properties of copolymer for different copolymer grades. All these studies used monofunctional initiators which gave a limited and low conversion.

In the hope of improving the process performance, optimization has been attempted in several studies. Since initiators are relatively expensive, there is always a need to minimize the specific initiator consumption rate but the same time it is desired to maximize polymer production. Marini and Georgakis (1984) did an interesting work on modeling, optimization and control of a vessel LDPE reactor. Yoon and Rhee (1985) applied the maximum principle to determine a suitable temperature that maximizes the exit monomer conversion in an LDPE tubular reactor. In an attempt to optimize LDPE

process, Mavridis and Kiparissides (1985) developed a systematic procedure for selecting the optimal initiator, transfer agent, and heat transfer control variables in a fixed-size high-pressure tubular reactor that maximized the reactor productivity at the desired product quality. They expressed a single objective function in terms of monomer conversion, number-average molecular weight and the polydispersity of the polymer. They considered three heating-cooling zones along the reactor length and found the optimal temperature profile, initiator and solvent concentrations. To solve the optimization problem they applied a global optimization method namely the complex method of sequential search optimization technique.

Also, Brandolin et al. (1991) examined the optimization problem for fixed-size LDPE tubular reactors using several operating policies. The usefulness of some of the optimal policies and the feasibility of practical implementation were also examined. Cervantes et al. (2000) presented a dynamic model for an entire LDPE plant with a mixture of ethylene, methane, butane and impurities. Based on the dynamic model of the whole plant, they determined optimal feed profiles to minimize the transient states generated during the switching between different steady states. Their model consisted of two parts, the first one corresponded to the reactor and the second to the rest of the plant. Lacunza et al. (2001) performed a parametric analysis on the tubular reactor with the purpose of finding the optimum operating conditions that maximized conversion, while keeping the product within desired specifications as regards polydispersity and long-chain branching indexes. Monomer, initiator and modifier flow rates, positions and temperatures of all feeds were analyzed to find the influence of these manipulated variables on the reactor productivity and product quality. They showed that splitting feed provides an increase in both conversion and polydispersity. They proved the modifier flow rate to be suitable control variable to keep the polydispersity within the desired value.

Asteasuain et al. (2001) provided a dynamic model of the high-pressure polymerization of ethylene in tubular reactor and formulated a dynamic optimization problem for studying start-up strategies. The optimization objectives were to maximize outlet conversion and optimize the time necessary for its stabilization while keeping product molecular properties between commercial ranges. The considered control variables were the initiator and telogen flow rates. The jacket temperature was considered to remain

constant at each zone between the inlet and output jacket temperatures of the corresponding zone. Yao et al. (2004) used a genetic algorithm (GA) to obtain the optimal jacket temperature profile required to maximize the polymer production. No requirements on the product properties were considered. The temperature of the heat-exchange fluid in jacket was used as control variable. Agrawal et al. (2006) presented a comprehensive model for an industrial low-density polyethylene (LDPE) tubular reactor. The model parameters were tuned using industrial data on the temperature profile, the monomer conversion and the number-average molecular weight at the end of the reactor, and estimates of the several side products from the reactor to get a good agreement of model predictions with industrial data. A two-objective optimization was considered for the LDPE reactor by imposing constraints on the molecular weight and the temperature of the reaction mass.

2.2 Difunctional initiators

Interest in the use of difunctional initiators for free radical polymerization began over three decades ago. Prisyazhnyuk and Ivanchev (1970) produced fundamental work on understanding the mechanism of polymerization with difunctional initiators. The authors examined the kinetics of several diperoxides having labile functional groups of differing thermal stability in the polymerization of styrene. The group of Choi and coworkers (1987, 1988) has written numerous papers starting with the employment of symmetrical difunctional initiators in the polymerization of styrene and developing a kinetic model.

Villalobos et al. (1991) modified the previous models using difunctional initiation as they found proposed model by Choi and coworkers had serious limitations for the prediction of molecular weights and molecular weight distributions at high conversions. Villalobos (1994) also extended the copolymerization theory to account for multiple initiation, propagation and termination cycles experienced by copolymer chains in free radical copolymerization with difunctional initiators using the pseudo-kinetic rate constants method. He developed a comprehensive model for the most general free radical copolymerization scheme, involving simultaneous and competitive statistical and donor-acceptor propagation mechanisms. He also evaluated the effects of multiple chain recombination during difunctionally initiated batch free radical copolymerization on

copolymer microstructure and compositional drift and introduced the concepts of effective instantaneous copolymer composition and number of segments per copolymer chain. The results of their study showed that batch time reduces for difunctional initiation reaction. In addition, based on the proposed comprehensive kinetic and micro-structure models, he designed and synthesis four different high T_g copolymers using difunctional initiators in bulk and suspension polymerization. Dhib et al. (2000) improved the CSTR model for styrene homopolymerization previously developed for difunctional initiators and tested the model validity on a large of data sets and incorporated the results into a computer simulation/database package. Recently, Scorah et al. (2004, 2005) have systematically investigated the use of a tetrafunctional peroxide initiator in the free radical polymerization of various homo- and co-polymer systems. These studies have shown that regardless of monomer type, higher rates of polymerization can be obtained with the tetrafunctional initiator when compared to its monofunctional counterpart. However, these investigations have also revealed that the effect on molecular weight is dependent upon the monomer. In the case of styrene, it was found that switching from a mono- to tetra-functional initiator produced no noticeable change in molecular weight. Yet with methyl methacrylate (MMA), the molecular weight was found to decrease when replacing a monofunctional initiator with a tetrafunctional one. In fact, it was observed that in the polymerization of MMA, equivalent results for the rate of polymerization and molecular weight could be obtained when using either the tetrafunctional initiator or the monofunctional initiator at a concentration four times that of the tetrafunctional. Also, Scorah et al (2006) proposed a new reaction mechanism for free radical polymerizations initiated by tetrafunctional initiators and described the kinetic model in detail. The mechanism is not solely limited to the polymerization of styrene but is applicable to other monomers such as MMA. Their model utilizes diffusion-controlled rate constants based on free volume theory and employs the method of moments to solve the various species balances.

In particular, Luft et al. (1985 a, b; 1988) set up a database of the most common peroxide initiators including difunctional initiators used in the production of polyethylene. They used over 20 initiators in experiments of LDPE production and assessed the initiator effectiveness on the basis of amount of each initiator consumed in the polymerization.

Their studies showed that in comparison with monofunctional initiators, difunctional initiators accelerate the polymerization rate and produce polymers of higher molecular weight at high temperature. Dhib and Al-Nidawy (2002) developed an unsteady kinetic model for polymerization of ethylene in an isothermal autoclave reactor using difunctional initiators. The simulation results from this model confirmed the trend of experimental data published by the group Luft et al. and also gave good prediction of the number average molecular weights and polydispersity of the polymer. Rate constants for three initiators were determined from data. It was shown that due to the dual functionality of difunctional peroxides, the ethylene conversion was about twice as much as that obtained with monofunctional peroxide, for only a half amount of the initiator concentration.

Continuing the works of Dhib and Al-Nidawy (2002) and Yao et al. (2004), a new kinetic scheme is proposed in this thesis to study copolymerization of ethylene and vinyl acetate (or butyl acrylate) using difunctional initiators in a tubular reactor with three zones of operation and multiple injection points for initiators and monomers.

The objective of this study can be summarized as follows:

- Development of Kinetic polymerization model for ethylene polymerization using difunctional initiators in non-isothermal tubular reactor with multiple feed injection points
- Development of kinetic model for ethylene copolymerization using difunctional initiators in non-isothermal tubular reactor with multiple feed injection points
- Determination by simulation of LCB and SCB related to difunctional peroxides
- Determination of optimal operating conditions of tubular reactor for homo- and copolymerization of ethylene using difunctional initiators

Chapter 3 Homo-polymerization of ethylene in autoclave and tubular reactors using difunctional initiators

The molecular and structural features of a polymer are directly related to the end-use properties of the final product. Therefore, controlling the polymer chain microstructure requires a thorough understanding of the polymerization kinetics and a quantitative description of the effect of the reactor operating conditions on the polymerization rate and molecular properties. Thus, there is an obvious need for the development of a comprehensive model for predicting the compositional and structural molecular properties of polymers produced in LDPE autoclave or tubular reactors. This chapter deals with LDPE polymerization modeling using difunctional initiators.

3.1 Reaction mechanism

By properly selecting an effective initiator, one can simultaneously achieve high monomer conversion and polymer molecular weight. The presence of two or more oxygen-oxygen bonds in multifunctional peroxides makes their kinetic decomposition into radical fragments quite particular. The splitting of oxygen bonds into free radicals may take several routes. Kim and Choi (1989) postulated the formation of a diradical $\cdot\text{O-R-O}\cdot$ from (un-) symmetrical peroxides, but there is not enough evidence to support the hypothesis. Nevertheless, two investigations (Luft and Seidl, 1985; Villalobos, Hamielec and Wood, 1991) using independent approaches indicated that an eventual formation of diradicals is unlikely to occur. In particular, for symmetrical peroxides in a high pressure and temperature process environment, Luft et al. (1985) investigated few schemes of decomposition into radical fragments producing hydrocarbons. The chemical structures of these initiators are shown in Appendix A.

Therefore, upon heating, a difunctional initiator decomposes into two radical species as follows:

Or symbolically:

Both initiator fragments $R_{in}^{\bullet}$ and $\tilde{R}_{in}^{\bullet}$ participate in the polymerization process and are capable of generating independent polymer chains. The polymer chain associated with the undecomposed peroxide radical $\tilde{R}_{in}^{\bullet}$ behaves as a 'macro' peroxide radical and subsequently become a part of the initiation step. The reaction mechanism for bulk free radical polymerization of ethylene using difunctional initiators is proposed below. M , I and P stand for the monomer (ethylene), difunctional initiator and the polymer (polyethylene), respectively.

Chemical initiation by difunctional peroxide:

Re-initiation:

Thermal initiation:

Propagation:

Termination by combination:

Transfer to monomer:

β - -scission to secondary radicals:

Intermolecular transfer (Backbiting):

Transfer to polymer:

Transfer to solvent:

Based on this scheme, the following species may be present in reaction mixture during a difunctionally initiated polymerization:

Table 3.1: Macromolecular Species

Symbols	Note
$R_r^\bullet : \bullet ---$	Live macromolecular radical of length r
$\tilde{R}_r^\bullet : \bullet --- \tilde{R}_n^\bullet$	Live re-initiator macromolecular of length r carrying undecomposed peroxide
$P_r : R --- R$	Dead polymer of length r
$\tilde{P}_r : R --- \tilde{R}$	Polymeric re-initiator of length r (carrying one undecomposed peroxide)
$\tilde{\tilde{P}}_r : \tilde{R} --- \tilde{R}$	Polymeric re-initiator of length r (carrying two undecomposed peroxide)

3.2 Kinetic rate constants

One of the most important issue in simulating a high pressure reactor is the selection of numerical values of kinetic rate constants. An interesting observation that can be made from a survey of modeling studies on ethylene polymerization is the significant discrepancy in the values of the rate constants. The disparity in the reported values of kinetic rate constants may be attributed to the complexity of the reaction mechanism, the large number of kinetic parameters to be identified experimentally, and the wide range of experimental conditions over which the kinetic parameters are estimated. A set of reaction rate constants was reported by Goto et al. (1981). The reported values were estimated from experimental measurements on monomer conversion, number- and weight- average molecular weights, amount of unsaturated double bonds, and total methyl content per 1000 carbon atoms. The measurements were obtained from an autoclave reactor operated under typical industrial conditions. In more recent studies by Zabisky et al. (1992), Brandolin et al. (1996) and Agrawal et al. (2006), the rate constants were estimated using industrial data. These researchers calculated the kinetic parameters using the temperature and conversion profiles and the molecular properties of the polymer. Because industrial data were involved, these workers did not provide complete information for proprietary reasons. The kinetic values estimated by Dhib and Al-Nidawy (2002) for ethylene polymerization using difunctional initiators have been applied in this study. The kinetic parameters are summarized in Table 3.2. The chemical nature of the chain end according to Villalobos (1994) is of no importance in the overall value of the

rate constants because the contribution of polymer radicals with chain length smaller than ten is negligible. Accordingly, the set of kinetic rate constants needed to evaluate the binary (co-) polymerization reaction rates with difunctional initiators reduces to that of the terminal model. Therefore:

$$\tilde{k}_{ij}=k_{ij} \quad i, j= 1,2 \quad (3.3)$$

$$\tilde{k}_{t\,ij}=\tilde{k}_{t\,ij}=k_{t\,ij} \quad (3.4)$$

Table 3.2: Reaction rate constants in ethylene polymerization

Rate Constant	$k = A \exp(-E/R_1T - \Delta vP/R_2T)$			
	A (1/s)	E (cal/mol)	Δv (cm ³ /mol)	Ref.
k_{th}	6.04×10^3	72,945	0.00	Dhib et al. (2002)
k_P	5.45×10^5	4210	-5.60	''
k_{tc}	4.35×10^8	3650	9.20	''
k_{tfm}	1.20×10^5	14,400	-20.00	''
k_{tp}	1.80×10^5	9400	0.00	''
k_b	3.25×10^5	7474	0.00	''
k_β	1.40×10^9	19,300	9.90	''
$k_{\beta'}/k_P$	1.034	5241	2.9	Verros et al. (1993)
k_{ts}	2.75×10^7	10370.5	-0.506	Mavridis (1985)

$$R_1=1.98 \text{ cal/mol K} \quad R_2=82 \text{ cm}^3 \text{ atm/mol K}$$

In this work one monofunctional initiator, dioctanoyl peroxide and two difunctional initiators 2,2-bis(tert-butylperoxy)butane (BU) and 2,5-dimethylhexane-2-*t*-butylperoxy-5-perpivalate (DHBPPI) are used for polymerization of ethylene and comonomers. The decomposition rate constants of these initiators were estimated by Dhib and Al-Nidawy (2002) and are reported in Table 3.3.

Table 3.3: Decomposition rate constants of peroxide initiators

Initiator	$k_{d1} = A_1 \exp(-E_1 / R_1 T - \Delta v_1 P / R_2 T)$		
	$k_{d2} = A_2 \exp(-E_2 / R_1 T - \Delta v_2 P / R_2 T)$		
	A_1, A_2 (1/s)	E_1, E_2 (cal /mol)	$\Delta v_1, \Delta v_2$ (cm ³ /mol)
Diocanoyl Peroxide	2.2925×10^{14}	30,131.70	5.9
	0	0	0
2,2-bis(tert-butylperoxy)- butane	1.812×10^{16}	42,307.83	28.0
	6.04×10^{13}	41,943.11	22.3
2,5-dimethylhexane-2- <i>t</i> - butylperoxy-5-perpivalate	1.812×10^{16}	43,037.28	25.0
	6.04×10^{17}	43,766.72	23.0

3.3 Dynamic modeling of an isothermal autoclave CSTR reactor

When modeling an isothermal autoclave reactor, it is assumed that the reactor volume, temperature and pressure remain constant. The reactor model consists of molar balances for all species, mainly the monomer, initiator, solvent and live and dead polymer radicals.

3.3.1 Reactor model

As the reaction proceeds, the monomer and the initiator are continuously consumed. The rate of consumption of each reactant is as follows:

Initiator decomposition rate:

$$\frac{d([I])}{dt} = -2k_{d1}[I] + q([I]_f - [I])/V \quad (3.5)$$

Rate of solvent consumption:

$$\frac{d([S]V)}{dt} = -k_s[S]V + q([S]_f - [S]) \quad (3.6)$$

Rate of monomer consumption:

Monomer consumption in transfer reaction is small compared to that in the propagation reaction. Therefore, the rate of monomer consumption is:

$$\frac{d([M])}{dt} = -R_p[M] + q([M]_f - [M])/V \quad (3.7)$$

Where q is the volumetric flow rate, V is the reactor volume and $[M]_f$ the feed monomer concentration. The rate of polymerization is defined by:

$$R_p = k_p \lambda_{tot} \quad (3.8)$$

Energy Balance:

In case of non-isothermal CSTR reactor, energy balance for the reactor mixture is given by:

$$\frac{d(T\rho c_p)}{dt} = (q/V)(T_f - T) + (-\Delta H_R)R_p + (UA_a/V)(T_c - T) \quad (3.9)$$

Where A_a is the area of the cooling jacket, T_f is the temperature of reactants fed to the reactor and U is the overall heat transfer coefficient between the jacket and the reactor. Energy balance for coolant in the jacket is:

$$\frac{d(T_c)}{dt} = (UA_a/V)(T - T_c)/\dot{m}_c c_{pc} \quad (3.10)$$

Since the autoclave reactor in this study is considered isothermal, the left hand side of energy equations (3.9) and (3.10) are set to zero.

3.3.2 Population balance moments

Unlike regular compounds with relatively small molecular weights, polymer samples are made up of a number of polymeric chains with different molecular weights. Therefore, the polymer sample is rather characterized by its average molecular weight. The method of moments affords a relatively simple method to calculate polymer averages. The moments of the molecular weight distribution are found by writing population balances on live and dead radicals of polymer chains, which are obtained below.

Moments of live polymer chains:

$$\lambda_i = \sum_{r=1}^{\infty} r^i [R_r^*] \quad (3.11)$$

$$\tilde{\lambda}_i = \sum_{r=1}^{\infty} r^i [\tilde{R}_r^*] \quad (3.12)$$

where i is 0, 1 or 2 for zeroth, first and second moment, respectively.

Moments of dead polymer chains:

$$\mu_i = \sum_{r=1}^{\infty} r^i [P_r] \quad (3.13)$$

$$\tilde{\mu}_i = \sum_{r=1}^{\infty} r^i [\tilde{P}_r] \quad (3.14)$$

$$\tilde{\tilde{\mu}}_i = \sum_{r=1}^{\infty} r^i [\tilde{\tilde{P}}_r] \quad (3.15)$$

3.3.3 Moments of live polymer balance

Writing a molar balance for primary radicals R_{in}^* and $\tilde{R}_{in}^*$ and applying steady-state hypothesis for short lived initiator radicals results in the following initiation:

$$R_I = 2f_1k_{di}[I] + f_2k_{d2}(\tilde{\mu}_0 + \tilde{\tilde{\mu}}_0) + 2k_{th}[M]^3 \quad (3.16)$$

$$\tilde{R}_I = 2f_1k_{di}[I] \quad (3.17)$$

where R_I is the rate of initiation for R_{in}^* and $\tilde{R}_I$ is the initiation rate for $\tilde{R}_{in}^*$. In above equations f_1 is the difunctional initiator efficiency and f_2 is the macro-initiator efficiency. The method of moments is a straightforward and compact way to determine the concentrations of live and dead polymer chains. For live radicals of polymer chains, applying a steady-state hypothesis gives rise to the following algebraic expressions for the radical concentrations:

$$\lambda_0 = \frac{R_I + \tilde{\lambda}_0(k_{ufm}[M] + k_{\beta} + k_{is}[S]) + f_2k_{d2}\tilde{\mu}_0}{k_{tc}\lambda_{tot}} \quad (3.18)$$

$$\tilde{\lambda}_0 = \frac{\tilde{R}_I + 2f_2k_{d2}\tilde{\tilde{\mu}}_0}{k_{tc}\lambda_{tot} + k_{ufm}M + k_{is}[S] + k_{\beta}} \quad (3.19)$$

where the total concentration of radical species includes radicals with the undecomposed peroxide group and radicals without any undecomposed peroxide group.

$$\lambda_{\text{tot}} = \lambda_0 + \tilde{\lambda}_0 = \sum_{r=1}^{\infty} [R_r^\bullet] + \sum_{r=1}^{\infty} [\tilde{R}_r^\bullet] \quad (3.20)$$

Rearranging equations (3.18) and (3.19) and adding those results in an analytical expression for total concentration of radicals:

$$\lambda_{\text{tot}} = \sqrt{\frac{R_I + \tilde{R}_I + f_2 k_{d2} (\tilde{\mu}_0 + 2\tilde{\mu}_0)}{k_{tc}}} \quad (3.21)$$

The equations for the first and second moments of live radicals are:

$$\lambda_1 = \frac{R_I + k_p M \lambda_0 + (k_{\text{tfm}}[M] + k_{ts}[S] + k_\beta) \lambda_{\text{tot}} + k_{tp} \lambda_0 (2\mu_2 + \tilde{\mu}_2) + f_2 k_{d2} \tilde{\mu}_1}{k_{tc} \lambda_{\text{tot}} + (k_{\text{tfm}}[M] + k_{ts}[S] + k_\beta + k_b) + k_{tp} (\mu_1 + \tilde{\mu}_1)} \quad (3.22)$$

$$\tilde{\lambda}_1 = \frac{\tilde{R}_I + k_p M \tilde{\lambda}_0 + k_{tp} \tilde{\lambda}_0 (\tilde{\mu}_2 + \mu_2) + 2f_2 k_{d2} \tilde{\mu}_1}{k_{tc} \lambda_{\text{tot}} + (k_{\text{tfm}} M + k_\beta + k_b + k_{ts}[S]) + k_{tp} (\mu_1 + \tilde{\mu}_1)} \quad (3.23)$$

$$\lambda_2 = \frac{R_I + k_p M (\lambda_0 + 2\lambda_1) + (k_{\text{tfm}}[M] + k_{ts}[S] + k_\beta) \lambda_{\text{tot}} + k_{tp} \lambda_0 (\mu_3 + \tilde{\mu}_3) + f_2 k_{d2} \tilde{\mu}_2}{k_{tc} \lambda_{\text{tot}} + (k_{\text{tfm}}[M] + k_{ts}[S] + k_\beta + k_b) + k_{tp} (\mu_1 + \tilde{\mu}_1)} \quad (3.24)$$

$$\tilde{\lambda}_2 = \frac{\tilde{R}_I + k_p [M] (\tilde{\lambda}_0 + 2\tilde{\lambda}_1) + k_{tp} \tilde{\lambda}_0 (\mu_3 + \tilde{\mu}_3) + 2f_2 k_{d2} \tilde{\mu}_2}{k_{tc} \lambda_{\text{tot}} + (k_{\text{tfm}}[M] + k_{ts}[S] + k_\beta + k_b) + k_{tp} (\mu_1 + \tilde{\mu}_1)} \quad (3.25)$$

3.3.4 Moments of dead polymer balances

Writing the molar balances on dead polymer chains of length r and applying the method of moments of chain length distribution results in the following expressions.

Dead polymer rising from primary radical:

$$\frac{d(V\mu_0)}{dt} = \left[\frac{1}{2} k_{ic} \lambda_0^2 + (k_{\text{tfm}}[M] + k_\beta + k_{ts}[S]) \lambda_0 \right] V - q\mu_0 \quad (3.26)$$

$$\begin{aligned} \frac{d(V\mu_1)}{dt} = & \left[k_{tc}\lambda_0\lambda_2 + (k_{tfm}[M] + k_{ts}[S])\lambda_1 + k_{\beta}(\lambda_1 - \lambda_0) + k_{tp}\mu_1(\lambda_1 + \tilde{\lambda}_1) \right. \\ & \left. - k_{tp}\lambda_{tot}\mu_2 \right] V - q\mu_1 \end{aligned} \quad (3.27)$$

$$\begin{aligned} \frac{d(\mu_2)}{dt} = & \left[k_{tc}(\lambda_1^2 + \lambda_0\lambda_2) + (k_{tfm}[M] + k_{ts}[S])\lambda_2 + k_{\beta}(\lambda_2 - 2\lambda_1 + \lambda_0) + \right. \\ & \left. k_{tp}\mu_1(\lambda_2 + \tilde{\lambda}_2) - k_{tp}\lambda_{tot}\mu_3 \right] V - q\mu_2 \end{aligned} \quad (3.28)$$

Dead polymer with one undecomposed peroxide:

$$\frac{d(V\tilde{\mu}_0)}{dt} = \left[k_{tc}\lambda_0\tilde{\lambda}_0 + (k_{tfm}[M] + k_{ts}[S] + k_{\beta})\tilde{\lambda}_0 - k_{d2}\tilde{\mu}_0 \right] V - q\tilde{\mu}_0 \quad (3.29)$$

$$\begin{aligned} \frac{d(V\tilde{\mu}_1)}{dt} = & \left[k_{tc}(\lambda_0\tilde{\lambda}_1 + \lambda_1\tilde{\lambda}_0) + (k_{tfm}[M] + k_{ts}[S])\tilde{\lambda}_1 + k_{\beta}(\tilde{\lambda}_1 - \tilde{\lambda}_0) + \right. \\ & \left. k_{tp}\tilde{\mu}_1(\lambda_1 + \tilde{\lambda}_1) - k_{tp}\lambda_{tot}\tilde{\mu}_2 - k_{d2}\tilde{\mu}_1 \right] V - q\tilde{\mu}_1 \end{aligned} \quad (3.30)$$

$$\begin{aligned} \frac{d(V\tilde{\mu}_2)}{dt} = & \left[k_{tc}(\lambda_2\tilde{\lambda}_0 + 2\lambda_1\tilde{\lambda}_1 + \lambda_0\tilde{\lambda}_2) + (k_{tfm}[M] + k_{ts}[S])\tilde{\lambda}_2 + \right. \\ & \left. k_{\beta}(\tilde{\lambda}_2 - 2\tilde{\lambda}_1 + \tilde{\lambda}_0) + k_{tp}\tilde{\mu}_1(\lambda_2 + \tilde{\lambda}_2) - k_{tp}\lambda_0\tilde{\mu}_3 - k_{d2}\tilde{\mu}_2 \right] V - q\tilde{\mu}_2 \end{aligned} \quad (3.31)$$

Dead polymer with two undecomposed peroxides, assuming no outflow:

$$\frac{d(V\tilde{\tilde{\mu}}_0)}{dt} = \left[\frac{1}{2}k_{tc}\tilde{\lambda}_0^2 - 2k_{d2}\tilde{\tilde{\mu}}_0 \right] V \quad (3.32)$$

$$\frac{d(V\tilde{\tilde{\mu}}_1)}{dt} = \left[k_{tc}\lambda_0\tilde{\lambda}_1 - 2k_{d2}\tilde{\tilde{\mu}}_1 \right] V \quad (3.33)$$

$$\frac{d(V\tilde{\tilde{\mu}}_2)}{dt} = \left[k_{tc}(\tilde{\lambda}_0\tilde{\lambda}_2 + \tilde{\lambda}_1) - 2k_{d2}\tilde{\tilde{\mu}}_2 \right] V \quad (3.34)$$

When transfers to polymer reactions are involved in the kinetic mechanism, the n -order polymer moment equation will depend on the $(n+1)$ order moment. Hence, the expressions for the second moment of the live and dead polymers include the third moment μ_3 , which is calculated using Hulburt and Katz (1964) approximation:

$$\mu_3 = \frac{\mu_2}{\mu_0 \mu_1} (2\mu_0 \mu_2 - \mu_1^2) \quad (3.35)$$

$$\tilde{\mu}_3 = \frac{\tilde{\mu}_2}{\tilde{\mu}_0 \tilde{\mu}_1} (2\tilde{\mu}_0 \tilde{\mu}_2 - \tilde{\mu}_1^2) \quad (3.36)$$

The dynamic model (3.26)-(3.36) is valid for a homopolymerization whether the initiator is mono- or difunctional. With monofunctional initiator the following conditions are set:

$f_2 = 0$, $\tilde{R}_I = 0$, $\tilde{\lambda} = 0$ (i.e. $\lambda_{\text{tot}} = \lambda_0$) and $k_{d2} = 0$; the rate of initiator de-fragmentation (3.5) becomes:

$$\frac{d([I])}{dt} = -k_{d1}[I] + q([I]_f - [I])/V \quad (3.37)$$

3.3.5 Molecular properties balances

An internal radical centre is a radical located on a backbone carbon atom and is formed by two reactions: transfer to polymer and backbiting. These internal radical centers can undergo all reactions that chain-end radicals do and then propagate leading to branching. The transfer to polymer leads to long chain branches (LCB). This reaction involves the transfer of reactivity from radical type j to a monomer type i unit in a dead polymer chain to form a new radical with an active centre somewhere along the chain. As a result, propagation leads to long chain branching.

$$\frac{1}{V} \frac{d(VC_{LCB})}{dt} = k_{LCB} (\lambda_0 + \tilde{\lambda}_0) (\mu_1 + \tilde{\mu}_1) \quad (3.38)$$

$$\text{where, } k_{LCB} = k_p[M] \times \frac{k_{tp}}{(k_p[M] + k'_p + k_{\text{ufm}}[M] + k_{ts}[S])} \quad (3.39)$$

In parallel, backbiting reaction leads to short chain branching (SCB). The radical activity in this case is transferred to a site along the same chain, which may propagate leaving a short chain branch.

$$\frac{1}{V} \frac{d(VC_{SCB})}{dt} = k_{SCB} (\lambda_0 + \tilde{\lambda}_0) \quad (3.40)$$

$$\text{where, } k_{SCB} = k_p[M] \times \frac{k_b}{(k_p[M] + k'_\beta + k_{tfm}[M] + k_{ts}[S])} \quad (3.41)$$

Besides, β – scission of secondary and tertiary radicals leads to the formation of vinyl and vinylidene groups as follows:

$$\frac{1}{V} \frac{d(VC_{VNL})}{dt} = k_{\beta'} (\lambda_0 + \tilde{\lambda}_0) \quad (3.42)$$

$$\frac{1}{V} \frac{d(VC_{VND})}{dt} = k_{\beta''} (\lambda_0 + \tilde{\lambda}_0) \quad (3.43)$$

Integration of reactor model leads to the calculation of ethylene concentration at any time and then conversion is calculated as:

$$\text{Conversion: } y(t) = \frac{[M]_0 - [M]_{(t)}}{[M]_0} \quad (3.44)$$

The molecular weight averages, short and long chain branching and vinyl and vinylidene groups frequencies are expressed in terms of leading moments of chain length distribution and the concentrations of C_{LCB} , C_{SCB} , C_{VNL} and C_{VND} .

Number average molecular weight:

$$\bar{M}_n(t) = \frac{Mw \{ \mu_1(t) + \tilde{\mu}_1(t) + \tilde{\tilde{\mu}}_1(t) + \lambda_1(t) + \tilde{\lambda}_1(t) \}}{\mu_0(t) + \tilde{\mu}_0(t) + \tilde{\tilde{\mu}}_0(t) + \lambda_0(t) + \tilde{\lambda}_0(t)} \quad (3.45)$$

Weight average molecular weight:

$$\bar{M}_w(t) = \frac{Mw \{ \mu_2(t) + \tilde{\mu}_2(t) + \tilde{\tilde{\mu}}_2(t) + \lambda_2(t) + \tilde{\lambda}_2(t) \}}{\mu_1(t) + \tilde{\mu}_1(t) + \tilde{\tilde{\mu}}_1(t) + \lambda_1(t) + \tilde{\lambda}_1(t)} \quad (3.46)$$

Long chain branches per 1000 carbon atoms:

$$(LCB/1000C) = 500C_{LCB} / (\mu_1 + \lambda_1) \quad (3.47)$$

Short chain branches per 1000 carbon atoms:

$$(SCB/1000C) = 500C_{SCB}/(\mu_1 + \lambda_1) \quad (3.48)$$

Vinylene double bonds per 1000 carbon atoms:

$$(VNL/1000C) = 500C_{VNL}/(\mu_1 + \lambda_1) \quad (3.49)$$

Vinylidene double bonds per 1000 carbon atoms:

$$(VND/1000C) = 500C_{VND}/(\mu_1 + \lambda_1) \quad (3.50)$$

3.3.6 Calculation of molecular weight distribution

The distribution of molecular sizes in a polymer chain is not completely defined by its central tendency. The breadth and shape of the distribution curve must also be known and this is determined most efficiently with the parameters defined from the moments of distribution. The ratio of $\bar{M}_n/\bar{M}_w$ is defined to measure the polydispersity of a sample. Using the calculated moments of each polymer, Wesslau distribution can be employed to construct molecular weight distribution (MWD) of polymer (Friis and Hamielec, 1975):

$$W(\ln(M)) = \frac{\exp\left(-\left(\ln(M) - \ln(\bar{M})\right)^2 / (2\sigma^2)\right)}{\sigma\sqrt{2\pi}} \quad (3.51)$$

$$\text{Where: } \sigma^2 = \ln\left(\frac{\bar{M}_w}{\bar{M}_n}\right) \quad (3.52)$$

$$\bar{M} = \bar{M}_n \exp\left(\frac{\sigma^2}{2}\right) \quad (3.53)$$

The two parameters σ^2 and $\bar{M}$ are only functions of molecular weight averages, thus equation (3.51) in conjunction with equations (3.45) and (3.46) can predict the molecular weight distribution for different amount of molecular weight averages.

3.4 Modeling of tubular LDPE reactor

A schematic diagram of the LDPE reactor is given in Figure 3.1. The tubular reactor is a thin tube and the flow is very fast and behaves like a plug flow. In practice, LDPE tubular reactors operate non-isothermally. The heat of reaction is partially removed through the

reactor wall by a heat transfer fluid which flows through the reactor jacket. Only approximately one-half of the heat of reaction is usually removed through the reactor wall. Due to non-isothermal operation of tubular reactor, the variation of thermodynamic and transfer properties of ethylene-polyethylene mixture along the reactor as functions of temperature, pressure and composition must be accounted for. The tubular reactor model includes mass, momentum and energy balances. The LDPE process is very fast. It is assumed that the transient period is very short. The steady state model is written using the axial length (z) as the independent variable, and differential equations are integrated along the reactor length.

To simplify the numerical solution of the reactor model equations the following dimensionless quantities are introduced:

$$- \text{Dimensionless length: } z = x / L \quad (3.54)$$

$$- \text{Dimensionless temperature : } \theta = (T - T_0) / T_0 \quad (3.55)$$

$$- \text{Dimensionless coolant temperature : } \theta_c = (T_c - T_0) / T_0 \quad (3.56)$$

$$- \text{Conversion : } y_j = (F_{j0} - F_j) / F_{j0} \quad (3.57)$$

where L is the reactor length, T_0 the reaction mixture temperature at the reactor inlet and F_j ($j = M, I, S$) the molar flow rate of monomer, initiator and solvent respectively. The molar flow rate F_j is expressed as follows:

$$F_j = (\pi D^2 / 4) u C_j \quad (3.58)$$

The concentration C_j ($j = M, I, S$) is related to the corresponding conversion y_j according to:

$$C_j = (u_0 / u) C_{j0} (1 - y_j) \quad (3.59)$$

Using dimensionless variables defined above, the tubular reactor model becomes:

Rate of reactants consumption:

$$\text{Initiator(s): } \frac{dy_{Ii}}{dz} = (L/u) [2k_{at} C_{I0} (1 - y_{Ii})] \quad (3.60)$$

$$\text{Monomer: } \frac{dy_m}{dz} = (L/u)(k_p + k_{tfm})\lambda_{\text{tot}}(1 - y_m) \quad (3.61)$$

$$\text{Solvent: } \frac{dy_{si}}{dz} = (L/u)k_{tsi}(1 - y_{si})\lambda_{\text{tot}} \quad (3.62)$$

Continuity equation:

$$\frac{du}{dz} = -(u/\rho) \left[T_0 (d\rho/dT)(d\theta/dz) + (d\rho/dy_m)(dy_m/dz) + (d\rho/dP)(dP/dz) \right] \quad (3.63)$$

Energy balance for the reaction mixture:

$$\begin{aligned} \frac{d\theta}{dz} = & \left[L(-\Delta H)_{r,T} (C_{M0}/T_0 \rho C_P) K_P (1 - y_m)/u \right] \lambda_{\text{tot}} + (4UL/Du_0 \rho C_P)(\theta_c - \theta) \\ & + (d \ln \rho^{-1}/d \ln T)_p (u/u_0 \rho C_P T_0)(dP/dz) \end{aligned} \quad (3.64)$$

Energy balance for fluid in the reactor jacket:

$$\frac{d\theta_c}{dz} = \pi D_o L U (\theta_c - \theta) / (\dot{m}_c c_{pc}) \quad (3.65)$$

Pressure drop:

The rates of reaction and thermodynamic properties of the reaction mixture depend on the reactor pressure which is expected to decrease along the reactor length. The pressure drop down to the pulse valve for turbulent flow in a tubular reactor is reasonably estimated by:

$$\frac{dP}{dz} = -L \left(2f\rho \frac{u^2}{D_i} + \rho u \frac{du}{dz} \right) \quad (3.66)$$

Where f is the fanning friction factor and is calculated by solving the non-linear equation:

$$(1/f)^{1/2} = 4 \log(\text{Re } f^{1/2}) - 0.4 \quad \text{for: } 2.1 \times 10^3 < \text{Re} < 5 \times 10^6 \quad (3.67)$$

The initial guess for numerical solution of the nonlinear equation for fanning friction factor is selected in the range: $(0.0791/\text{Re}^{1/4}) < f < 0.01$, which according to Zabisky et al. (1992) is the typical value for friction factor under LDPE reactor conditions.

3.4.1 Live polymer moment equations

Temporary radicals have very short residence time and are consumed instantaneously. Assuming that the quasi-steady approximation for the live radical chains λ_i and $\tilde{\lambda}_i$ is still valid and neglecting the velocity gradient (du/Ldz) in balance equations on live polymer radicals, expressions already developed in section 3.3.2 are reasonably accepted to estimate λ_i and $\tilde{\lambda}_i$ as long as the overall molar flow remains high. In this case, the monomer, initiator and solvent concentrations for tubular reactor in equations are:

$$[M] = C_{M0} (u_0/u) (1 - y_m) \quad (3.68)$$

$$[I] = C_{I0} (u_0/u) (1 - y_I) \quad (3.69)$$

$$[S] = C_{S0} (u_0/u) (1 - y_S) \quad (3.70)$$

where u_0 is the inlet velocity and C_{M0} , C_{I0} and C_{S0} are the reactants concentrations in feed.

3.4.2 Polymer model

As stated in sub-section 3.3.4, the polymer model can be formulated by taking a molar balance of all species P , $\tilde{P}$ and $\tilde{\tilde{P}}$ and then utilizing the statistical mechanics method of moments over a very large random number of dead polymer chains. The method of moments reduces the infinite system of molar balances to a low order system of differential equations that can be easily solved to give the concentrations of macromolecular species at any position along a tubular reactor.

On the basis of the postulated kinetic mechanism for difunctional initiators, the following moment rates for dead polymer chains are described.

Dead polymer rising from primary radical:

$$\begin{aligned} \frac{d\mu_0}{dz} = & \left\{ L \left[k_{tc} \lambda_0^2 / 2 + (k_{tfm} C_{M0} (u_0/u) (1 - y_m) + k_p + k_b \right. \right. \\ & \left. \left. + k_{ts} (u_0/u) C_{S0} (1 - y_S) \right) \lambda_0 \right] - \mu_0 (du/dz) \right\} / u \end{aligned} \quad (3.71)$$

$$\frac{d\mu_1}{dz} = \left\{ L \left[k_{tc} \lambda_0 \lambda_1 + (k_{tfm} C_{M0} (u_0/u) (1 - y_m) + k_p + k_b \right. \right. \\ \left. \left. + k_{ts} (u_0/u) C_{S0} (1 - y_s) \right) \lambda_1 + k_{fp} \left((\lambda_1 + \tilde{\lambda}_1) \mu_1 - \lambda_{tot} \mu_2 \right) \right] - \mu_1 (du/dz) \right\} / u \quad (3.72)$$

$$\frac{d\mu_2}{dz} = \left\{ L \left[k_{tc} (\lambda_0 \lambda_2 + \lambda_1^2) + (k_{tfm} C_{M0} (u_0/u) (1 - y_m) + k_p + k_b \right. \right. \\ \left. \left. + k_{ts} (u_0/u) C_{S0} (1 - y_s) \right) \lambda_2 + k_{fp} \left((\lambda_2 + \tilde{\lambda}_2) \mu_1 - \lambda_{tot} \mu_3 \right) \right] - \mu_2 (du/dz) \right\} / u \quad (3.73)$$

Dead polymer with one undecomposed peroxide:

$$\frac{d\tilde{\mu}_0}{dz} = \left\{ L \left[k_{tc} \lambda_0 \tilde{\lambda}_0 - k_{d2} \tilde{\mu}_0 + (k_{tfm} C_{M0} (u_0/u) (1 - y_m) + k_p \right. \right. \\ \left. \left. + k_b + k_{ts} (u_0/u) C_{S0} (1 - y_s) \right) \tilde{\lambda}_0 \right] - \tilde{\mu}_0 (du/dz) \right\} / u \quad (3.74)$$

$$\frac{d\tilde{\mu}_1}{dz} = \left\{ L \left[k_{tc} (\lambda_0 \tilde{\lambda}_1 + \lambda_1 \tilde{\lambda}_0) - k_{d2} \tilde{\mu}_1 + (k_{tfm} C_{M0} (u_0/u) (1 - y_m) + k_p \right. \right. \\ \left. \left. + k_b + k_{ts} (u_0/u) C_{S0} (1 - y_s) \right) \tilde{\lambda}_1 + k_{fp} \left((\lambda_1 + \tilde{\lambda}_1) \tilde{\mu}_1 - \lambda_{tot} \tilde{\mu}_2 \right) \right] - \tilde{\mu}_1 (du/dz) \right\} / u \quad (3.75)$$

$$\frac{d\tilde{\mu}_2}{dz} = \left\{ L \left[k_{tc} (\lambda_2 \tilde{\lambda}_0 + 2\lambda_1 \tilde{\lambda}_1 + \lambda_0 \tilde{\lambda}_2) - k_{d2} \tilde{\mu}_2 + (k_{tfm} C_{M0} (u_0/u) (1 - y_m) \right. \right. \\ \left. \left. + k_p + k_b + k_{ts} (u_0/u) C_{S0} (1 - y_s) \right) \tilde{\lambda}_2 + k_{fp} \left((\lambda_2 + \tilde{\lambda}_2) \tilde{\mu}_1 - \lambda_{tot} \tilde{\mu}_3 \right) \right] - \tilde{\mu}_2 (du/dz) \right\} / u \quad (3.76)$$

Dead polymer with two undecomposed peroxide:

$$\frac{d\tilde{\tilde{\mu}}_0}{dz} = \left\{ L \left[k_{tc} \tilde{\tilde{\lambda}}_0^2 - 2k_{d2} \tilde{\tilde{\mu}}_0 \right] - \tilde{\tilde{\mu}}_0 (du/dz) \right\} / u \quad (3.77)$$

$$\frac{d\tilde{\tilde{\mu}}_1}{dz} = \left\{ L \left[k_{tc} \tilde{\tilde{\lambda}}_0 \tilde{\tilde{\lambda}}_1 - 2k_{d2} \tilde{\tilde{\mu}}_1 \right] - \tilde{\tilde{\mu}}_1 (du/dz) \right\} / u \quad (3.78)$$

$$\frac{d\tilde{\tilde{\mu}}_2}{dz} = \left\{ L \left[k_{tc} (\tilde{\tilde{\lambda}}_0 \tilde{\tilde{\lambda}}_2 + \tilde{\tilde{\lambda}}_1^2) - 2k_{d2} \tilde{\tilde{\mu}}_2 \right] \right\} / u \quad (3.79)$$

3.4.3 Molecular properties balances

As aforementioned, the short and long chain branching can have an important effect on polymer properties. The more short chain branches incorporated along the polymer chain,

the lower will be the polymer density, while long chain branches affect the rheological properties. Long chain branches are produced by transfer to polymer reaction. Thus, the total concentration of long chain branches is expressed below:

$$\frac{dC_{LCB}}{dz} = \left[Lk_{LCB}\lambda_{tot}(\mu_1 + \tilde{\mu}_1) - C_{LCB} \left(\frac{du}{dz} \right) \right] / u \quad (3.80)$$

The short chain branches are produced by backbiting, therefore the number of short chain branches produced is:

$$\frac{dC_{SCB}}{dz} = \left[Lk_{SCB}\lambda_{tot} - C_{SCB} \left(\frac{du}{dz} \right) \right] / u \quad (3.81)$$

k_{LCB} and k_{SCB} are given by (3.39) and (3.41).

Unsaturated vinyl and vinylidene groups concentrations are:

$$\frac{dC_{VNL}}{dz} = \left[Lk_{\beta'}\lambda_{tot} - C_{VNL} \left(\frac{du}{dz} \right) \right] / u \quad (3.82)$$

$$\frac{dC_{VND}}{dz} = \left[Lk_{\beta''}\lambda_{tot} - C_{VND} \left(\frac{du}{dz} \right) \right] / u \quad (3.83)$$

Integrating the reactor model and the polymer model simultaneously gives profile of the species concentrations and the polymer moments along the reactor length.

The conversion of monomer along the reactor is expressed by:

$$y_m(z) = \frac{[M]_0 - [M]_{(z)}}{[M]_0} \quad (3.84)$$

The molecular weight averages, the SCB and LCB as well as the amount of double bonds per 1000 carbon atoms can be expressed in terms of moments of the total chain length distributions and the concentrations of C_{LCB} , C_{SCB} , C_{VNL} and C_{VND} .

Weight average molecular weight:

$$M_w(z) = \frac{Mw_m \{ \mu_2(z) + \tilde{\mu}_2(z) + \tilde{\mu}_2(z) + \lambda_2(z) + \tilde{\lambda}_2(z) \}}{\mu_1(z) + \tilde{\mu}_1(z) + \tilde{\mu}_1(z) + \lambda_1(z) + \tilde{\lambda}_1(z)} \quad (3.85)$$

Number average molecular weight:

$$M_n(z) = \frac{Mw_m \{ \mu_1(z) + \tilde{\mu}_1(z) + \tilde{\tilde{\mu}}_1(z) + \lambda_1(z) + \tilde{\lambda}_1(z) \}}{\mu_0(z) + \tilde{\mu}_0(z) + \tilde{\tilde{\mu}}_0(z) + \lambda_0(z) + \tilde{\lambda}_0(z)} \quad (3.86)$$

Long chain branches per 1000 carbon atoms:

$$(\text{LCB}/1000\text{C}) = 500 C_{\text{LCB}} / (\mu_1 + \tilde{\mu}_1 + \tilde{\tilde{\mu}}_1) \quad (3.87)$$

Short chain branches per 1000 carbon atoms:

$$(\text{SCB}/1000\text{C}) = 500 C_{\text{SCB}} / (\mu_1 + \tilde{\mu}_1 + \tilde{\tilde{\mu}}_1) \quad (3.88)$$

Vinylene double bonds per 1000 carbon atoms:

$$(\text{VNL}/1000\text{C}) = 500 C_{\text{VNL}} / (\mu_1 + \tilde{\mu}_1 + \tilde{\tilde{\mu}}_1) \quad (3.89)$$

Vinylidene double bonds per 1000 carbon atoms:

$$(\text{VND}/1000\text{C}) = 500 C_{\text{VND}} / (\mu_1 + \tilde{\mu}_1 + \tilde{\tilde{\mu}}_1) \quad (3.90)$$

3.4.4 Physical and transport properties

Correlations for physical and transport properties are listed in Table 3.4. The physical and transport properties are functions of pressure, temperature and composition of the reaction mixture and vary along the axial location. The overall heat transfer coefficient U was updated at every axial location in the reactor zones. Specific volume, heat capacity and thermal conductivity of the reaction mixture are calculated by summing up the properties of each component weighted with the weight fraction of monomer and polymer. The accuracy of these physical properties was also checked using HYSYS software.

Table 3.4: Physical and transport properties

Property	Expression	Reference
$V_{M,E}$	$\{ 3.7994 - 0.2610978 \ln(P) - 0.6944404 \ln(T) + 0.0632416 \ln(T) \times \ln(P) \}^{-1}$	Feucht et al.(1985)

$V_{P,E} = 9.61 \times 10^{-7} + 7.0 \times 10^{-10} T - 5.3 \times 10^{-11} P$	Feucht et al (1985).
$\rho = \frac{1+0.028 \times [C_M](V_P - V_M)}{V_P}$	Gupta et al. (1985)
$C_P = 0.518(1 - y_m) + (1.041 + 8.3 \times 10^{-4} T) y_m$	Kalyon et al. (1994)
$-\Delta H_E = (84.185 \times 10^3 + 0.209(T - 273) + 0.105P) / 4.1868$	Kiparissides(1993).
$k \text{ (cal/cm.sec.K)} = 5 \times 10^{-4} (1 - y_m) + 3.5 \times 10^{-4} y_m$	Kiparissides (1993)
$\left[(\eta - \eta^0) \xi + 1 \right]^{0.25} = \frac{1.023 + 0.2336 \rho_r + 0.58533 \rho_r^2 - 0.40758 \rho_r^3 + 0.09332 \rho_r^4}{\rho_r^4}$	Reid et al (1997).
$\xi = 10^7 \left(\frac{T_c}{M' \times (9.869 P_c)^4} \right)^{1/6}$	<div> $T_c \text{ (K)} : \text{Critical temperature}$ $P_c \text{ (MPa)} : \text{Critical pressure}$ $M' \text{ (kg / kmol)} : \text{Ethylene Molecular weight}$ </div> Reid et al. (1997)
$\eta^0 \xi = 4.61 T_r^{0.618} - 2.04 \exp(-0.449 T_r) + 1.94 \exp(-4.058 T_r) + 0.1 \text{ for } 0.1 < \rho_r < 3$; all viscosities in Pa.s	Poling et all (2001).
$\eta_s = \eta \exp \left[2 + 0.001 a_v \left(\frac{\mu_1}{\mu_0} \right)^{0.556} \times \mu_1 + \frac{E_v}{R} \left(\frac{1}{T} - \frac{1}{423} \right) \right],$ all viscosities in Pa.s	Kiparissides et al.(1993)
$E_v = -(500 - 560 \mu_1)$ $a_v = 0.018$	Kiparissides et al. (1993) Kiparissides et al. (1993)
$U^{-1} = h_i^{-1} + h_w^{-1}$ $h_i = k \text{Nu} / D_i$, inside heat transfer coefficient $h_w = 0.03$	Kiparissides et al. (1993) Kiparissides et al. (1993) Mavridis et al.(1985)
$\text{Nu} = 0.166 \left(\text{Re}^{2/3} - 125 \right) \text{Pr}^{0.33} \left[1 + \left(\frac{D_i}{L} \right)^{2/3} \right], \text{ (for Re} < 10000 \text{)}$	Zabisky et al.(1992)
$\text{Nu} = 0.026 \text{Re}^{0.8} \text{Pr}^{0.33}, \text{ (for Re} > 10000 \text{)}$ $\text{Pr} = C_p \eta_s / k$ $\text{Re} = \rho u D_i / \eta_s$	Zabisky et al. (1992) Kiparissides et al. (1993) Kiparissides et al. (1993)

The density of the gas-phase mixture is assumed to depend on composition, where the molar volumes of the pure components are functions of temperature and pressure. It is assumed that there is no excess volume of mixing. In order to account for the variation of density along the reactor, which is required to solve the continuity and energy balances, the derivative of density with respect to reactor length was calculated as a function of temperature, pressure and composition of the reaction mixture. The resulting equation for density variation is:

$$\frac{d\rho}{dz} = T_0 \left(\frac{d\rho}{dT} \right) \left(\frac{d\theta}{dz} \right) + \left(\frac{d\rho}{dy_m} \right) \left(\frac{dy_m}{dz} \right) + \left(\frac{d\rho}{dP} \right) \left(\frac{dP}{dz} \right) \quad (3.91)$$

where derivatives of reaction mixture density were calculated using the correlation of Gupta et al. (1985) for density:

$$\frac{d\rho}{dT} = \frac{0.028 \times [C_M] V_P \times \left(\frac{dV_P}{dT} - \frac{dV_M}{dT} \right) - \frac{dV_P}{dT} (1 + 0.028 \times [C_M] (V_P - V_M))}{V_P^2} \quad (3.92)$$

$$\frac{d\rho}{dP} = \frac{0.028 \times [C_M] V_P \times \left(\frac{dV_P}{dP} - \frac{dV_M}{dP} \right) - \frac{dV_P}{dP} (1 + 0.028 \times [C_M] (V_P - V_M))}{V_P^2} \quad (3.93)$$

$$\frac{d\rho}{dy_m} = -0.028 \times [C_M]_0 \times (u_0/u) \times \frac{(V_P - V_M)}{V_P} \quad (3.94)$$

The variations of specific volume of monomer and polymer with temperature, pressure and composition were derived using correlations for ethylene and polyethylene specific volume in Table 3.4 and are summarized as follows:

$$\frac{dV_{M,E}}{dT} = \frac{T^{-1} \times (0.6944404 - 0.0632416 \ln P)}{(3.7994 - 0.2610978 \ln P - 0.6944404 \ln T + 0.0632416 \ln T \times \ln P)^2} \quad (3.95)$$

$$\frac{dV_{P,E}}{dT} = 7 \times 10^{-7} \quad (3.96)$$

$$\frac{dV_{M,E}}{dP} = \frac{P^{-1} \times (0.2610978 - 0.0632416 \ln T)}{(3.7994 - 0.2610978 \ln P - 0.6944404 \ln T + 0.0632416 \ln T \times \ln P)^2} \quad (3.97)$$

$$\frac{dV_{P,E}}{dP} = -5.3 \times 10^{-11} \quad (3.98)$$

3.5 Multiple feed tubular reactor

LDPE high-pressure tubular reactors usually have a main feed stream consisting of ethylene, solvent and peroxide initiators. Sometimes, there are other injection points of initiators and monomer along the reactor as shown in Figure 3.1. Depending on the number of side feed injections, reactor is divided to two or three sections. Each section consists of heating/ cooling jacket zones for the control of the reaction temperature and removal of excess heat. A tubular LDPE reactor consists of a spiral wrapped metallic pipe with a large length-to-diameter ratio from 250:1 to 12000:1 and operates at temperature up to 300°C and pressure up to 2800atm. The total length of the reactor ranges from 500 to 1500m and the internal diameter does not exceed 60mm. Steam is used in the first portion of the reactor to heat up the cold feed to the desired initial temperature. Lower jacket temperatures are used in the next portion of the reactor to remove the heat due to the polymerization. About half of the amount of heat evolved in an ethylene polymerization reaction is removed by a coolant flowing in jacket around the reactor (usually water). Therefore, a non-isothermal reactor operation is experienced, even though heat removal in a tube reactor is much better than in an autoclave reactor.

In industry, normally a single reactor can produce several kinds of polyethylene of different molecular characteristics, making them appropriate for specific final usages. In order to simulate tubular reactors with multiple feed points (injecting initiator, monomer, and solvent), appropriate equations for instantaneous mixing are also required.

Figure 3.1: Tubular reactor with three zones

Figure 3.2: Schematic description of mixing point

3.5.1 Mixing point equations

Computation of the mixture conditions after the injection is quite delicate. When simulating the operation of a tubular reactor with lateral feed streams, mass, momentum and energy balances should be solved simultaneously to find velocity and temperature of the reaction mixture as well as concentrations of components after injection point. Lateral feedings are supposed to be at the same pressure as the reaction mixture at the point of injection. The parameters used to describe mixing point equations are shown in figure 3.2.

Momentum balance:

$$u_f \rho_f = u_o \rho_o + \frac{28\bar{M} + Mw_s \bar{S} + Mw_I \bar{I}}{A} \quad (3.99)$$

In which ρ_f is the density of the mixture and it is given by:

$$\rho_f = \frac{1 + 0.028[M]_f (V_{Pf} - V_{Mf})}{V_{Pf}} \quad (3.100)$$

where,

$$V_{Mf} = \left\{ 3.7994 - 0.2610978 \ln(P_f) - 0.6944404 \ln(T_f) + 0.0632416 \ln(T_f) \times \ln(P_f) \right\}^{-1} \quad (3.101)$$

$$V_{Pf} = 9.61 \times 10^{-7} + 7.0 \times 10^{-10} T_f - 5.3 \times 10^{-11} P_f \quad (3.102)$$

Mass balances for each component:

$$\text{Monomer: } u_f [M]_f = u_o [M]_o + \frac{10^3 \bar{M}}{A}, [M]_o = (u_o / u_o) C_{M0} (1 - y_{mo}) \quad (3.103)$$

$$\text{Initiator: } u_f [I]_f = u_o [I]_o + \frac{10^3 \bar{I}}{A}, [I]_o = (u_o / u_o) C_{I0} (1 - y_{Io}) \quad (3.104)$$

$$\text{Solvent: } u_f [S]_f = u_o [S]_o + \frac{10^3 \bar{S}}{A}, [S]_o = (u_o / u_o) C_{S0} (1 - y_{so}) \quad (3.105)$$

Similarly,

$$u_f [X]_f = u_o [X]_o \quad (3.106)$$

for [SCB], [LCB], [Vinyl] and [Vinylidene] and $\lambda_i, \tilde{\lambda}_i, \mu_i, \tilde{\mu}_i, \tilde{\mu}_i$, for $i = 0, 1, 2$.

Energy balance:

The local temperature results from an enthalpy balance between the main flow and the lateral feeding.

$$C_{Pf} T_f = \frac{A \rho_o u_o C_{po} T_o + (28\bar{M} + Mw_s \bar{S} + Mw_I \bar{I}) C_{pi} T}{A \rho_o u_o + 28\bar{M} + Mw_s \bar{S} + Mw_I \bar{I}} \quad (3.107)$$

where C_{Pf} is the heat capacity of the reaction mixture after injection point:

$$C_{pf} = 0.518w_m + (1.041 + 8.3 \times 10^{-4} T_f)w_p \quad (3.108)$$

Very little initiator and solvent are added, hence their contributions to the density and the heat capacity are neglected. So, the heat capacity of the lateral stream is assumed to be the same as pure ethylene and equal to $C_{pi} = 0.518 \text{ cal/g.}^\circ\text{K}$.

In equation (3.108) w_m and w_p are the weight fractions of monomer and polymer after the mixing point. The weight fractions w_m and w_p are calculated by performing a mass balance on the total mass of monomer fed to the reactor up to the mixing point:

$$w_m = \frac{\bar{M} + [M]_o u_o A/1000}{\bar{M} + [M]_o u_o A/1000 + (C_{M0}u_o - [M]_o u_o) A/1000} \quad (3.109)$$

$$w_p = 1 - w_m = \frac{(C_{M0}u_o - [M]_o u_o) A/1000}{\bar{M} + [M]_o u_o A/1000 + (C_{M0}u_o - [M]_o u_o) A/1000} \quad (3.110)$$

The nonlinear equations (3.99), (3.103) and (3.107) are solved simultaneously by Gauss-Newton method for $[M]_f$, u_f and T_f , respectively. The monomer conversion at any position is defined as:

$$y_m \text{ (Accumulated monomer conversion)} = \left(1 - \frac{u[M]A/1000}{u_o C_{M0}A/1000 + \bar{M}} \right) \times 100 \quad (3.111)$$

where $\bar{M}$ is the molar flow rate of monomer injected to reactor and C_{M0} is the concentration of monomer at inlet to each section of the reactor.

3.6 Results and discussion

First, the model for free radical bulk polymerization of ethylene with difunctional initiators is compared with experimental data collected from literature. Then, the performance of a LDPE tubular reactor with difunctional initiators is investigated via sensitivity analysis to variations of process input variables, such as initiator type, initiator injection modes, reactor jacket and so forth. The reactor and polymer model was solved with the help of a built-in Matlab function, *ode15s*, which is a variable order solver based

on the numerical Gear's method designed for stiff differential equations. The stiffness characteristic is a result of the wide disparity in the rates of the various kinetic steps.

3.6.1 Model validation with CSTR data

The proposed kinetic model, Equations (3.5)-(3.43) describes the behavior of ethylene polymerization in a CSTR autoclave reactor. The validity of the model for ethylene polymerization using difunctional initiators is investigated by comparing predictions with data collected on an isothermal autoclave reactor (Luft and Seidl, 1985; Luft and Dorn, 1988). A reactor of volume 15 mL operating at 1700 bar pressure was considered in simulation to compare ethylene conversion data versus reaction temperature for different residence times. The operating conditions of the simulation are summarized in Table 3.5.

Table 3.5: LDPE autoclave reactor operating conditions

Peroxide	Initiator Name	Temperature (°C)	Initiator concentration (ppm mol)	Residence time (Sec)
I	Diocanoyl	100- 200	40	65
II	2,2-bis(tert-butylperoxy)- butane (BU)	200-300	10, 20	40
III	2,5-dimetyl hexane -2- <i>t</i> - butylperoxy-5-perpivalate (DHBPI)	200-300	5, 10, 20	60

Prediction of ethylene conversion using a CSTR model versus temperature are plotted in Figures 3.3-3.8 and compared with data for different initiator types. According to the data collected (Luft et al., 1977), ethylene conversion with peroxide I of initial concentration of 40 ppm remains very low for moderate temperatures around 110°C and then accelerates quickly to a maximum value of 15% corresponding to a temperature around 165°C above which the conversion starts dropping gradually (Figure 3.3). High temperatures favor the side reactions, which lowers the number of primary radicals, thus hindering the initiation of polymer chains. This conversion trend with temperature was observed experimentally and confirmed by the CSTR kinetic model. The model follows

the data trend and gives a maximum conversion prediction of 15.62 % at temperature 156°C, and then it follows the data closely for higher temperatures after peak. Similarly, model predictions are in good agreement with data for two difunctional initiators (Luft and Seidl, 1985; Luft and Dorn, 1988). Figure 3.4 shows comparison of model predictions with experimental data of Luft and Seidl (1985) for difunctional peroxide II, carried out in temperature range 200°C to 300°C, with a concentration of 20 mol ppm and residence time of $\theta_r = 40s$. Ethylene conversion increases up to a maximum of 21.8 % corresponding to 264°C and then falls down for higher temperatures. Data conversion reaches a maximum of 20.27% at 268.9°C. A deviation error about 0.3% between model predictions and experimental data for conversion indicates an acceptable model prediction. In comparison with peroxide I, only half amount of peroxide II was required to get higher conversion with a reduced reaction time of $\theta_r = 40$ sec, but at the expense of higher temperature. To make another comparison, the simulation was repeated for peroxide II with a concentration of 10 mol ppm. The model predictions shown in Figure 3.5 deviate from experimental data for temperatures less than 245°C, but for higher temperatures satisfactory prediction exists. In comparison with monofunctional peroxide I, only a quarter of difunctional peroxide II was enough to get similar maximum conversion.

In the third run, the productivity of difunctional initiator III, with concentrations of 25, 10, 5 mol ppm have been examined. Comparison of model predictions with the experimental data of Luft and Dorn (1988) is illustrated through Figures 3.6-3.8. For concentration of 5 mol ppm the maximum predicted conversion is 23.86% at a temperature of 267°C, which is close to experimental value 23.41% but at a temperature of 254.9°C. As a whole, the model in this case, does not represent the data at low temperatures quite well. However in comparison with peroxide I, only quarter of difunctional peroxide III concentration, yields twice the conversion of monofunctional initiator. The simulation also was repeated for 25 and 10 mol ppm concentrations. The model follows the data quite well for higher concentrations of peroxide III, but slightly deviates for lower temperatures. Also, ethylene conversion is about twice as much as that obtained with monofunctional peroxide, for only a half amount of the initial initiator concentration, which is due to the dual functionality of difunctional peroxide. In addition,

the conversion also increases with increasing initiator concentration in the feed. High productivity of peroxide III can be related to its higher efficiency ($f=0.8$) and rate of decomposition compared to peroxide II ($f=0.65$). The number average molecular, $\bar{M}_n$ for both difunctional initiators were compared with experimental data of Luft and Seidl (1985) as illustrated in Figure 3.9. No data is available for $\bar{M}_w$. For elevated temperatures there is good agreement between data and predictions. To investigate the effect of initiator type on molecular properties of the polymer, the polydispersity index (PDI) was obtained for Dioctanoyl and two other difunctional initiators. As Figure 3.10 shows PDI for difunctional initiators is higher than for monofunctional. Zimmermann and Pollok (1998) observe similar results. The maximum PDI for peroxide III is 3.35, for peroxide II, 2.93 and for dioctanoyl, 2.5.

3. 6. 2 Simulation of a LDPE isothermal autoclave reactor

Three dimension plots in Figures 3.11-3.13 show the evolution of ethylene conversion versus time and temperatures. Dioctanoyl initiator is more suited for temperatures not exceeding 170°C, whereas difunctional initiators are recommended for a higher temperature range 240-290°C.

Molecular weight distributions obtained with dioctanoyl peroxide and the difunctional initiators at temperature 230°C are compared in Figure 3.14. Difunctional peroxides produce polymer chains with wider molecular weight distribution which can be attributed to the sequential decomposition of the functional groups that are likely to increase branching frequencies.

The breadth of the polymer is of great important as it affects the end-product properties. Polyethylene product with wide MWD is beneficial to specific applications such as extrusion coating.

Figure 3.3: Prediction and data conversion versus temperature for ethylene bulk polymerization using dioctanoyl with initial concentration of 40 ppm $P=1700$ bar and $\theta_r = 65$ sec.

Figure 3.4: Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,2-bis(tert-butylperoxy)butane with initial concentration of 20 mol ppm $P=1700$ bar and $\theta_r = 40$ sec.

Figure 3.5: Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,2-bis(tert-butylperoxy)butane with initial concentration of 10 mol ppm P=1700 bar and $\theta_r = 40$ sec .

Figure 3.6: Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate with initial concentration of 5 mol ppm P=1700 bar and $\theta_r = 60$ sec .

Figure 3.7 Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate with initial concentration of 10 mol ppm P=1700 bar and $\theta_r = 60$ sec .

Figure 3.8: Prediction and data conversion versus temperature for ethylene bulk polymerization using 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate with initial concentration of 25 mol ppm P=1700 bar and $\theta_r = 60$ sec .

Figure 3.9: Average molecular weight predictions and data versus temperature for ethylene bulk polymerization. For initiators 2,2-bis(tert-butylperoxy)-butane (BU) and 2,5-dimethyl hexane-2-t-butylperoxy-5-perpivalate (DHBPI) each with $[I]=20$ mol ppm, $P=1700$ bar and $\theta_r = 60$ sec.

Figure 3.10: Predictions of polydispersity index of LDPE versus temperature. For diocanoyl $[I]=40$ ppm, 2,2-bis(tert-butylperoxy)-butane (BU) and 2,5-dimethyl hexane-2-t-butylperoxy-5-perpivalate (DHBPI) each with $[I] = 20$ ppm.

Figure 3.11: Prediction of conversion versus time and temperatures for dioctanoyl with initial concentration of 40 mol ppm, $P=1700$ bar, $\theta_r = 65$ sec.

Figure 3.12: Prediction of conversion versus time and temperatures for 2,2-bis(tert-butylperoxy)-butane with initial concentration of 10 mol ppm, $P=1700$ bar, $\theta_r = 40$ sec.

Figure 3.13: Prediction of conversion versus time for different temperatures for 2,5-dimethyl hexane -2-t-butylperoxy-5-perpivalate with initial concentration of 10 mol ppm, $P=1700$ bar, $\theta_r = 60$ sec .

Figure 3.14: Prediction of molecular weight distribution for Ethylene bulk polymerization using dioctanoyl, 2,2-bis(tert-butylperoxy)-butane and 2,5-dimethyl hexane -2-t-butylperoxy-5-perpivalate, with initial concentrations $[I]= 20$ ppm, $P=1700$ bar, $T=230^{\circ}\text{C}$ and $\theta_r = 60$ sec .

3.6.3 Simulation of tubular reactor

For simulation studies each reactor section is divided into three zones, pre-heating, reaction and cooling zones. For simplicity, the jacket temperature was considered constant at each zone. Asteasuain et al. (2001) have discussed that considering constant jacket temperature can give reasonably good prediction of the temperature profile of the reaction mixture. Besides, constant jacket temperature reduces computation time to solve numerically the coupled set of ODEs of the reacting fluid and the energy balance equations of the counter-currently jacket side flowing fluid. In this study, a preheating zone length covers 30% of the total reactor length, whereas the reaction zone covers 37% and the cooling zone 33%. Upon injecting an initiator stream, the polymerization boosts up instantaneously and the reaction temperature attains a ceiling limit, corresponding to the depletion of the initiator and termination of the reaction. In the cooling section, no reaction takes place and the reaction mixture is cooled by the coolant flowing through the reactor jacket. Temperature control is necessary for safe operation of tubular polyethylene reactors, since explosive de-polymerization reactions can occur when temperatures exceed 300°C. The initiator type is an important factor influencing the peak temperature of the reaction mixture. In industrial reactors, the temperature profiles and in particular peak temperature values are controlled by manipulation of feed temperature and pressure, telogen and initiator flow rates as well as their compositions. Keeping the peak temperature within a certain range ensures the production of a desired polymer grade. The remaining operating conditions of the tubular reactor are summarized in Table 3.6.

Table 3.6: Design features and operating conditions of LDPE tubular reactor

Length (m)	1390
Internal Diameter (cm)	5.25018
Inlet pressure (bar)	2400
Inlet temperature (°C)	120
Mass flow-rate of feed (kg/s)	11

Volumetric flow of the inlet feed is:

$$Q_0 = F_0 / \rho_{M,E} \quad (3.112)$$

where F_0 is the inlet mass flow rate. The inlet velocity u_0 is:

$$u_0 = Q_0 / A \quad (3.113)$$

Thus, the inlet monomer concentration is:

$$[M_0] = (F_0 / 28) \times (A u_0)^{-1} = \rho_{M,E} / 28 \quad (3.114)$$

From the above equations it is concluded that the concentration of the inlet feed is equal to its molar density.

3.6.3.1. Isothermal analysis

The effect of temperature on the performance of tubular reactor was investigated upon operating the tubular reactor isothermally at two temperatures 160°C and 270°C which correspond to the optimal operating temperatures for monofunctional peroxide I and difunctional peroxide II and III, respectively. Each initiator feed concentration is kept at 20 mol ppm. It was observed that at 160°C, conversion for peroxide I reaches 13.35% (Figure 3.15) with no initiator left. However, since the difunctional peroxide II and III require higher temperature to decompose, no reaction occurs at 160°C. Figure 3.16 show no monomer conversion occur (peroxide II: 0.53 % and peroxide III: 0.38%). However, the evolution of the average molecular weight averages in Figure 3.17 is due to thermal initiation.

At 270°C, difunctional initiators II and III decompose and conversion reaches 24.15% and 32.87%, respectively (Figure 3.18). Conversely, monofunctional peroxide I is depleted at 270°C, before any reaction can occur and so ethylene conversion remains as low as 0.63%. Again, even though at 270°C, dioctanoyl does not contribute to the polymerization, polymer is still produced via thermal initiation (Figure 3.20).

Alternatively, running the simulation at a constant temperature 230°C, all peroxides approximately give the same ethylene conversion. In accordance with Zimmermann and Pollok (1998) experimental results, the final average molecular weights are higher for peroxide II and III as shown in Figure 3.21.

Figure 3.15: Ethylene conversion profiles for different initiators at constant temperature 160 °C.

Figure 3.16: Initiator conversion profiles at constant temperature 160 °C.

Figure 3.17: Average molecular weights at constant temperature 160°C.

Figure 3.18: Ethylene conversion profiles at constant temperature 270°C.

Figure 3.19: Initiators conversion profiles at constant temperature 270°C.

Figure 3.20: Average molecular weights at constant temperature 270°C.

Figure 3.21: Comparison of number- and weight- average molecular weights along the tubular reactor for different initiators at constant temperature 230°C.

3.6.2.2. Non-isothermal analysis

Figures 3.22-3.29 illustrate model predictions obtained with peroxides I, II and III. For a clear and good assessment of the peroxides performance in polymerizing ethylene, an SQP optimization procedure was accomplished to determine the optimal wall temperature for each zone that gives a maximum conversion. The optimization procedure was attempted to determine optimal jacket temperature for each zone and initiator concentration that maximizes ethylene conversion provided that maximum reaction temperature does not exceed 300°C. The optimization procedure computes the jacket temperature and the initiator concentration required to maximize conversion (Table 3.7).

The optimal dioctanoyl concentration resulting from optimization was 27.3 ppm, while for peroxide II and III it was 14.8 and 10.4 ppm, respectively. The optimal dioctanoyl concentration is twice and three times that of difunctional initiators II and III respectively. High decomposition temperature of peroxide II and III generates more primary radicals which boost the polymerization rate causing the reaction temperature to rise further. The temperature profile in Figure 3.22 demonstrates that the peak

temperature for difunctionals occurs further in the reactor. Figure 3.23 shows that the maximum conversion does not exceeds 13.35% for dioctanoyl, whereas it reaches 19.4% and 22.9% for peroxide II and peroxide III, respectively.

Variation of polydispersity and average molecular weights $\bar{M}_n$ and $\bar{M}_w$ are illustrated in Figures 3.24 and 3.25. The operating conditions also affect the average molecular weights which of course decrease with increasing temperature. Initiator decomposition is more dependent on temperature than chain growth, whereas chain termination is little affected. Thus, the population of live free radicals increases and more monomer molecules readily react with the radicals to form polymer chains. Higher polydispersity index for difunctional initiators indicates that the polymer produced is more branched as shown in Figures 3.26 and 3.27 which illustrate profiles of long- and short chain branching, respectively. Vinylene and vinylidene groups follow similar trends (Figures 3.28 and 3.29). The concentration of these groups for difunctional initiators is higher than that for monofunctional peroxide, because existing several labile groups within a polymer molecule can increase the branching frequency. The introduction of long chain branching is advantageous for polymer processing as it improves melt strength (Scorah, 2006). On the other hand short chain branches are undesirable as these groups leads to lower crystallinity, density and tensile strength. Unsaturated vinylene and vinylidene groups could make the final product susceptible to cracking due to oxide formation (Agrawal et al. 2006). Thus, difunctional peroxides are not always advantageous.

Table 3.7: Optimal operating conditions for LDPE tubular reactor

Initiator	T _{1,Jacket} (°C)	T _{2,Jacket} (°C)	T _{3,Jacket} (°C)	[I] (ppm)
Dioctanoyl	107.6	150.12	101.7	27.3
2,2-bis(tert-butylperoxy)-butane (BU)	223.35	211.65	193.16	14.8
2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate (DHBPII)	232.9	209.45	185.4	10.4

Figure 3.22: Temperature profiles of different initiators.

Figure 3.23: Conversion profiles of different initiators.

Figure 3.24: Comparison of polydispersity along the tubular reactor for different initiators.

Figure 3.25: Comparison of number- and weight- average molecular weights a) versus reactor length b) versus conversion.

Figure 3.26: Prediction of long chain branching frequency for different initiators.

Figure 3.27: Prediction of short chain branching frequency for different initiators.

Figure 3.28: Prediction of vinylene group frequency for different initiators.

Figure 3.29: Prediction of vinylidene group frequency for different initiators.

3.6.2.3 Effect of multiple feed on polymer properties in tubular reactor

The model previously developed for multiple feed tubular reactor is used to analyze the influence of splitting monomer and initiator feed on reactor productivity and polymer quality. Product quality is measured in terms of molecular weight, polydispersity and branching indexes.

In this investigation, the product quality and reactor productivity are compared for three cases and the effect of split ratio on conversion is studied. In the first case, the monomer and initiator feeds are divided into a main stream introduced at the reactor entrance, and two lateral streams with ratio $R=50\%$, 25% and 25% with respect to the overall monomer and initiator feed. In the second case, the initiator feed is split into two intermediate injections with ratio $R=50\%$, 25% and 25% with respect to overall initiator feed and in last case no injections are considered. The operating conditions for this simulation are summarized in Table 3.8. The distributions of monomer and initiator feeds are demonstrated in Figures 3.30 and 3.31.

Table 3.8: Operating conditions for multiple feed tubular reactor

Overall monomer feed flow rate (kg/s)	11
Initiator	2,2-bis(tert-butylperoxy)-butane
Overall initiator molar flow rate (mol/sec)	7.8572×10^{-4}
Feed temperature (°C)	120
Monomer side feed temperature (°C)	80
Jacket temperature (°C)	240
Lateral feeds positions (dimensionless)	0.3, 0.67
Pressure (bar)	2400
Scenario 1: monomer and initiator injections at 2 points	
Scenario 2: initiator injections at 2 points	
Scenario 3: monomer and initiator fed at front stream only	

Figure 3.32 shows temperature profiles for three operation scenarios. For scenario 1, three temperature peaks are recorded and for the second scenario, two moderate temperature peaks. Only one temperature peak is recorded for scenario 1. The use of intermediate monomer injections leads to cold shot of the reaction mass. Figure 3.33 shows that separating the initiator and monomer injections provide an increase in conversion. The final monomer conversion in scenario 1, 2 and 3 goes up to 23%, 21% and 15%, respectively. The sudden fall of the overall ethylene conversion after monomer injection is due to the injection of the quenching stream.

Figure 3.34 shows the initiator consumption in three cases, scenario 2 and 3 allow the initiator concentration to refresh at two locations, which in turn keeps the polymerization going on. For scenario 3, the initiator concentration decreases to zero at about 45% of the reactor length. Figure 3.35 shows the corresponding initiator conversion profiles.

Figures 3.36 illustrates that the weight average molecular weights increases to 10233 upon splitting monomer feed, whereas when there is no injection, average molecular weight drops to 95810 and in case of initiator splitting, 93010. The increase in average molecular weights upon splitting monomer feed is due to increasing conversion and long chain branching formation. Trends of changing polydispersity and long chain branching are shown in Figure 3.37 and 3.38, respectively. Splitting the feed into at least 2 injection

points help to increase polydispersity and long chain branching. Variation of Reynolds Number is depicted in Figure 3.39. Reynolds number changes from 100,000 to 300,000 which proves that under flow conditions of this simulation the plug flow assumption is fully justified.

Figure 3.30: Monomer mass flow rate for a) monomer and initiator injections at $z=0.3$ and $z=0.67$, b) no injection and c) initiator injection at two points at $z=0.3$ and $z=0.67$.

Figure 3.31: Initiator molar flow rate for a) monomer and initiator injections at $z=0.3$ and $z=0.67$, b) no injection and c) initiator injection at two points at $z=0.3$ and $z=0.67$.

Figure 3.32: Predicted temperature profile

Figure 3.33: Predicted ethylene conversion

Figure 3.34: Prediction of initiator concentration

Figure 3.35: Prediction of initiator conversion

Figure 3.36: Predicted number and weight average molecular weights a) versus reactor length b) versus conversion.

Figure 3.37: Predicted polydispersity

Figure 3.38: Predicted long chain branching frequency

Figure 3.39: Reynolds number

Chapter 4 Co-polymerization of ethylene in autoclave and tubular reactors using difunctional initiators

The synthesis of linear and branched low density polyethylene (LDPE) and its copolymers by free-radical reactions is of significant economic importance to the polymer industry. In fact, polymerization of ethylene and co-monomer like vinyl acetate, acrylic or methacrylic acid, and methyl, butyl or ethyl acrylate can lead to the production of polar polymers which usually exhibit crystallinity and yield strength lower than LDPE grades and are used for applications requiring flexibility, toughness, stress-cracking resistance, and adhesion to coatings.

In this chapter, the kinetic mechanism of copolymerization of ethylene with a co-monomer using difunctional initiators is developed by application of the pseudo-kinetic rate constants method. First, the model is developed for an isothermal autoclave reactor dynamics and it is then extended to non-isothermal tubular reactor. The net production and consumption rate functions of all molecular species present in the polymerization system are derived. The number and weight average molecular weights and copolymer composition, conversion, SCB and LCB frequencies are calculated in terms of the leading moments of live and dead copolymer chains.

Let I , M_i , $R^\bullet$ and P designate the initiator, the monomer/comonomer i , the live polymer radical and the dead polymer. A kinetic scheme for a copolymerization system initiated with a difunctional peroxide is presented as follows:

subscripts $i, j=1, 2$ stand for monomer type and r and s for chain length.

Chemical Initiation:

Re-initiation:

Thermal Initiation:

Propagation:

Termination by combination:

Transfer to Monomer:

Intermolecular transfer to polymer:

β – scission to secondary radicals :

Intermolecular Transfer (Backbiting):

Transfer to solvent:

4.1 Pseudo-kinetic rate constant approach

The kinetic equations for a copolymerization system can be simplified using pseudo-kinetic rate constants. The pseudo-kinetic rate constants are the rate constants for each elementary reaction weighted by the mole fractions of monomer or various macroradicals in the reactor. First some fractions are calculated based upon the composition of the reactor contents and the kinetic constants.

The reactivity ratios for propagation are defined as:

$$r_1 = k_{p11} / k_{p12} \quad (4.1)$$

$$r_2 = k_{p22} / k_{p21} \quad (4.2)$$

where k_{pij} is the elementary propagation rate constant when monomer type j adds to polymer radical of type i .

The mole fraction of each monomer type in the reaction mixture is given by:

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad (4.3)$$

$$f_2 = 1 - f_1 \quad (4.4)$$

where $[M_i]$ is molar concentration of monomer i .

Copolymer composition is one of the most important factors that affects the properties of copolymer. It is well known that copolymer composition drift occurs in free radical copolymerization reactor due to the different reactivity ratios of two monomers. The mole fraction of monomer i chemically bound in copolymer is defined in two ways as stated below:

Accumulated copolymer composition:

$$\bar{F}_1 = \frac{\psi_1}{\psi_1 + \psi_2} \quad (4.5)$$

$$\bar{F}_2 = 1 - \bar{F}_1 \quad (4.6)$$

where ψ_1 is moles of monomer 1 bound in polymer. ψ_1 and ψ_2 can be found by performing a mass balance on the monomer.

Instantaneous copolymer composition:

$$F_1 = \frac{(r_1 - 1)f_1^2 + f_1}{(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} \quad (4.7)$$

$$F_2 = 1 - F_1 \quad (4.8)$$

The mole fraction of a growing polymer chain is given by:

$$\phi_1 = \frac{k_{P21}f_1}{k_{P21}f_1 + k_{P12}f_2} \quad (4.9)$$

$$\phi_2 = 1 - \phi_1 \quad (4.10)$$

Table 4.1 gives the relations for determining the apparent rate of free radical copolymerization from individual rate constants of each monomer (Xie and Hamielec 1993a, b and Villalobos, 1994). As previously stated in Chapter 3 (Equations 3.3 and 3.4), it is assumed that the chemical nature of the chain end is of very little importance in the overall value of the rate constants and so the rate constants for radicals with undecomposed peroxide groups can be equal to that radicals emerging from primary peroxide. The necessary condition for the applicability of the pseudo-kinetic rate constants is that the mole fraction of any radical type be independent of chain length, that is: $\phi_1 = \phi_{1,i} = \phi_{2,i} = \dots = \phi_{r,i}$. It has been proved that this condition is fully satisfied when the number average chain length is greater than few hundreds (Hamielec et al. 1987; Tobia 1990).

Table 4.1: Apparent rate constants for free-radical copolymerization

Thermal initiation of monomer	$k_{th} = k_{th1}f_1^3 + k_{th2}f_2^3$
Propagation	$k_p = k_{p11}\phi_1f_1 + k_{p21}\phi_2f_1 + k_{p12}\phi_1f_2 + k_{p22}\phi_2f_2$
Termination by disproportionation	$k_{td} = k_{td11}\phi_1^2 + 2k_{td12}\phi_1\phi_2 + k_{td22}\phi_2^2$
Termination by combination	$k_{tc} = k_{tc11}\phi_1^2 + 2k_{tc12}\phi_1\phi_2 + k_{tc22}\phi_2^2$
Overall bimolecular termination rate constant	$k_t = k_{tc} + k_{td}$
Transfer to monomer	$k_{ym} = k_{ym11}\phi_1f_1 + k_{ym21}\phi_2f_1 + k_{ym12}\phi_1f_2 + k_{ym22}\phi_2f_2$
Transfer to polymer	$k_{tp} = k_{tp11}\phi_1\bar{F}_1 + k_{tp21}\phi_2\bar{F}_1 + k_{tp12}\phi_1\bar{F}_2 + k_{tp22}\phi_2\bar{F}_2$
Backbiting	$k_b = k_{b11}\phi_1F_1 + k_{b21}\phi_2F_1 + k_{b12}\phi_1F_2 + k_{b22}\phi_2F_2$
β – scission of terminal radicals	$k_\beta = k_{\beta1}\phi_1 + k_{\beta2}\phi_2$
β – scission of internal radicals	$k'_\beta = k'_{\beta1}\bar{F}_1 + k'_{\beta2}\bar{F}_2$
Transfer to chain transfer agent	$k_{ts} = k_{ts1}\phi_1 + k_{ts2}\phi_2$

It should be noted that the use of pseudo-kinetic rate constants for reactions involving polymer chains is not strictly correct, since the composition of the chains will vary with monomer conversion. The use of F_i and $\bar{F}_i$ is to take into account for compositional drift. However, the deviation errors introduced are uncertain for large extents of compositional drift and ascertain the apparent rate constants. Since ethylene conversion is relatively low, and the comonomer composition is small, the compositional drift is virtually insignificant, especially for ethylene/vinyl acetate, where $r_1 \approx r_2 \approx 1$. The use of pseudo-kinetic rate constants is merely an approximation for the branching reactions (transfer to polymer and backbiting), but it is a good representation for propagation, termination and transfer reactions.

The high-pressure reactor behavior is very sensitive to the numerical values of the kinetic rate constants. It is important to point out that data is very limited on ethylene/vinyl

acetate polymerization in high-pressure gas phase reactors. In case of ethylene homopolymerization complete data set including temperature and pressure dependencies can be found in literature but information on β -scission, backbiting and chain transfer rate constants for vinyl acetate is not available to our knowledge. The rate constants for ethylene are reported in Table 3.2 in Chapter 3. Table 4.2 gives the reaction rate constants for high pressure free radical polymerization of vinyl acetate. Becker and Busch (1998) and Boxtel and Busch (2001) suggested that the value of each cross transfer to monomer or polymer rate constant can be estimated by dividing the corresponding value of the homo-transfer rate constant by the respective reactivity ratio value. This was based on the assumption that the transfer activity relative to propagation may not be affected by the composition of the macro-radicals but rather only controlled by the reactivity of the macro-radicals. Thus, cross transfer constants are expressed as:

$$k_{\text{tfm},12} = k_{\text{tfm},11} / r_1 \quad (4.11)$$

$$k_{\text{tfm},21} = k_{\text{tfm},22} / r_2 \quad (4.12)$$

$$k_{\text{tp}12} = k_{\text{tp}11} / r_1 \quad (4.13)$$

$$k_{\text{tp}21} = k_{\text{tp}22} / r_2 \quad (4.14)$$

Cross termination and cross backbiting rate constants are assumed to be equal to those in homopolymerization. However, the reactivity ratios involving a gaseous comonomer become more complex since they appear to be pressure dependent. Both Burkhart and Zutty (1963) and Brown and Ham (1964) determined reactivity ratios for ethylene/vinyl acetate polymerization for bulk and solution at very high pressures (12000-15000 psig) and suggested that $r_{\text{Eth}} \approx r_{\text{VAc}} \approx 1$ at high pressure, but deviations occur at low pressure. Due to similar reactivity ratios at elevated pressures, ethylene/vinyl acetate copolymers can be produced with desired copolymer composition to satisfy the targeted final polymer properties requirement. The copolymer structure may range from completely amorphous to a semi-crystalline material.

Table 4.2: Kinetic rate constants for vinyl acetate

		A (L/ mol.s)	E/R (K)	ΔV (cm ³ /mol)	Reference
Propagation	k_p	1.47×10^7	2490	-10.7	Beuermann et al., (2001)
Termination by combination	k_{tc}	2.7×10^{10}	1409	-	Kiparissides et al., (2003)
Transfer to monomer	k_{tm}/k_p	1.42×10^{-2}	2700	-	Kiparissides et al., (2003)
Transfer to polymer	k_{tp}/k_p	1.088×10^4	3170	-	Kiparissides et al., (2003)
Reactivity Ratios:	Ethylene		r_1	1.06	Brandrup et al., (1999)
	Vinyl acetate		r_2	1.09	Brandrup et al., (1999)

Ethylene/butyl acrylate copolymerization has also been studied in this work in order to determine the effect of different transfer reactions such as transfer to monomer, polymer and scission reactions on the properties of copolymer. Accurate experimental determination of the reactivity ratios is a prerequisite to a realistic simulation analysis of copolymerization of ethylene and a comonomer. Buback and co-workers (1996) determined the reactivity ratio for high pressure ethylene/butyl acrylate copolymerization as a function of temperature (Equations (4.15) and (4.16)). They showed that with increasing temperature, the reactivity ratio of ethylene increases slowly but the reactivity ratio of butyl acrylate decreases at a very fast rate. Table 4.3 summarizes the ethylene/butyl acrylate kinetic rate constants.

$$\ln r_E = -1.139 - 917.3/T \quad (4.15)$$

$$\ln r_{BA} = -3.591 + 2428/T \quad (4.16)$$

Table 4.3: Kinetic rate constants for buthyl acrylate

		A (L/ mol.s)	E/R (K)	ΔV (cm ³ /mol)	Reference
Propagation	k_p	1.81×10^7	2092.8	-11.7	Meyer and Keurentjes (2005)
Termination by combination	k_{tc}	5.1×10^8	481.09	16	Meyer and Keurentjes (2005)
Transfer to monomer	k_{tm}	2.9×10^5	7786	-	Hamer and Ray (1986)
Transfer to polymer	k_{tp}	59.93	4156	-	Hamer and Ray (1986)
Reactivity Ratios:	Ethylene		r_1	Equation (4.26)	Buback et al. (1996)
	Butyl acrylate		r_2	Equation (4.27)	Buback et al. (1996)

4.2 Polymer reactor model

Using the pseudo-kinetic rate constant approach for binary copolymerization (Table 4.1), the models for autoclave and tubular reactor developed in Chapter 3 have been extended in this thesis to simulate ethylene copolymerization.

4.2.1 Ethylene copolymerization model in an isothermal autoclave reactor

With the aid of pseudo-kinetic approach, the dynamic model (3.5)–(3.43) can be easily extended to an autoclave reactor to describe copolymerization. Monomer concentration is the summation of monomers concentrations in the reaction mixture:

$$[M] = [M_1] + [M_2] \quad (4.17)$$

Other balance equations necessary for modeling a co-polymerization system are the molar balances for monomers type 1 and 2 as well as the molar balances for monomers bounded in copolymer. These equations are described as follows:

Rate of change of monomer concentration:

In free radical polymerization, monomer consumption in initiation and transfer reactions is negligible in comparison with the monomer consumed in the propagation reaction. Thus, for each monomer species:

$$\frac{d([M_1])}{dt} = -(k_{p11}\phi_1 + k_{p21}\phi_2)\lambda_{tot}[M_1] + q([M_1]_f - [M_1])/V \quad (4.18)$$

$$\frac{d([M_2])}{dt} = -(k_{p22}\phi_2 + k_{p12}\phi_1)\lambda_{tot}[M_2] + q([M_2]_f - [M_2])/V \quad (4.19)$$

where $[M_i]_f$ denotes the feed concentration of monomers 1 and 2 .

Mole Balances for Monomer 1 and 2 bound in copolymer:

The rates of monomer 1 and 2 bound in copolymer can be calculated by performing a molar balance on the monomer consumed in the reaction to form polymer chains.

$$\psi_{1(t)} = [M_1]_0 - [M_1]_{(t)} \quad (4.20)$$

$$\psi_{2(t)} = [M_2]_0 - [M_2]_{(t)} \quad (4.21)$$

Integration of equations (4.18) and (4.19) allows the computation of the accumulated copolymer composition $\bar{F}_1$ and $\bar{F}_2$, which is required in updating the rate constants of transfer to polymer, k_{tp} and β – scission of internal radicals, k'_β .

Energy Balance:

In case of non-isothermal autoclave reactor, the energy balance for copolymerization is:

$$\begin{aligned} \frac{d(T\rho c_{pm})}{dt} = & (q/V)(T_f - T) + [(-\Delta H_{R1})(k_{p11}\phi_1 + k_{p21}\phi_2) + (-\Delta H_{R2})(k_{p12}\phi_1 + k_{p22}\phi_2)]\lambda_{tot} \\ & + (UA_a/V)(T_c - T) \end{aligned} \quad (4.22)$$

Where A_a is the area of cooling and T_f is the temperature of reactants in the feed to the CSTR reactor, U is the overall heat transfer coefficient between the jacket and the reactor. The energy balance for the coolant in the jacket is:

$$\frac{dT_c}{dt} = (UA_a/V)(T - T_c)/m_c c_{pc} \quad (4.23)$$

As previously stated in Chapter 3, transfer to polymer leads to long chain branches (LCB). This reaction involves the transfer of reactivity from radical type j to i type monomer unit in a dead polymer chain to form a radical with the active centre

somewhere along the chain. In presence of monomer, propagation leads to long chain branching.

R' denotes an internal radical. Then propagation occurs:

Variation of Long chain branching per copolymer molecule in a continuous stirred tank copolymerization reactor is given below:

$$\frac{d(C_{LCB})}{dt} = \sum_{i=1}^2 \sum_{j=1}^2 \left(k_{tpij} \varphi_i F_j (\mu_1 + \tilde{\mu}_1) + k_{dpij} \varphi_i (\mu_0 + \tilde{\mu}_0) \right) \lambda_{tot} \quad (4.24)$$

Backbiting leads to short chain branching (SCB). For the formation of short chain branches via backbiting, the radical activity is transferred to a site along the same chain, and this site may propagate leaving behind a short chain branch on the main branch:

and then the propagation proceeds:

Combining molar balances with the moments approach gives:

$$\frac{d(C_{SCB})}{dt} = (k_{b1} \varphi_1 + k_{b2} \varphi_2) (\lambda_0 + \tilde{\lambda}_0) \quad (4.25)$$

A complete description of the derivation of these equations is provided in Appendix.

Similarly for other traces of vinylene and vinyliden:

$$\frac{d(C_{VNL})}{dt} = k_{\beta'} (\lambda_0 + \tilde{\lambda}_0) \quad (4.26)$$

$$\frac{d(C_{VND})}{dt} = k_{\beta''} (\lambda_0 + \tilde{\lambda}_0) \quad (4.27)$$

4.2.2 Modeling copolymerization reaction in tubular reactor

In addition to the CSTR modeling approach previously presented, momentum balance has to be incorporated as well as an update of the thermodynamic and transfer properties. The set of equations (3.60)-(3.83) in Chapter 3 remain valid to model a copolymerization system. Additional considerations are needed for monomer and energy balances in the tubular reactor.

Rate of change of conversion of monomer 1 and 2:

$$\frac{dy_{m1}}{dz} = (L/u) (k_{P11}\varphi_1 + k_{P21}\varphi_2) \lambda_{tot} (1 - y_{m1}) \quad (4.28)$$

$$\frac{dy_{m2}}{dz} = (L/u) (k_{P12}\varphi_1 + k_{P22}\varphi_2) \lambda_{tot} (1 - y_{m2}) \quad (4.29)$$

Mole Balances for monomer 1 and 2 bound in copolymer

$$\frac{d([\psi_1])}{dz} = (L/u) (k_{p11}\varphi_1 + k_{p21}\varphi_2) \lambda_{tot} [M_1] \quad (4.30)$$

$$\frac{d([\psi_2])}{dz} = (L/u) (k_{p12}\varphi_1 + k_{p22}\varphi_2) \lambda_{tot} [M_2] \quad (4.31)$$

Energy balance of the copolymerization system:

$$\begin{aligned} \frac{d\theta}{dz} = & \frac{L}{\rho u T_0 c_p} \left(\sum_{i=1}^2 (-\Delta H_{Ri}) \sum_{j=1}^2 k_{Pij} \varphi_i C_{m0j} (1 - y_{mj}) \right) \lambda_{tot} + (4UL/Du_0 \rho C_p) (\theta_c - \theta) \\ & + (d \ln \rho^{-1} / d \ln T)_p (u/u_0 \rho C_p T_0) (dP/dz) \end{aligned} \quad (4.32)$$

Physical and thermodynamic properties:

The intensive thermodynamic properties (specific volume, specific heat and thermal conductivity) of the reaction mixture are calculated by a simple addition rule:

$$P_m = \sum_{i=1}^N w_i P_i \quad (4.33)$$

P_m is the property of the mixture, w_i is the weight fraction of the i component, and P_i denotes the corresponding property of the i component. The physical and heat transfer properties of ethylene and polyethylene are given in Table 3.4, Chapter 3. The properties of vinyl acetate and butyl acrylate are summarized in Table 4.4 and Table 4.5, respectively.

Table 4.4: Physical and thermodynamic properties of vinyl acetate

Property Expression	Reference
$V_{M,VAc} = (5.346 \times 10^{-2} + 1.33 \times 10^{-4} T) / (Mw_{VAc} \times 10^{-3})$	Hamer and Ray (1986)
$V_{P,VAc} = (5.608 \times 10^{-2} + 5.41 \times 10^{-5} T) / (Mw_{VAc} \times 10^{-3})$	Hamer and Ray (1986)
$Cp_{M,VAc} = 0.4716$	Teymour and Ray (1989)
$Cp_{P,VAc} = 0.3453 + 9.55 \times 10^{-4} (t - 25)$	Teymour and Ray (1989)
$k_{M,VAc} = 5.4242 \times 10^{-4}$	Albert and Luft (1999)
$k_{P,VAc} = 4.3 \times 10^{-4}$	Hamer and Ray (1986)
$-\Delta H_{VAc} = 20899$	Brandrup J. et al. (1998)
<hr/>	
$Mw_{VAc} = 86.09 \text{ (g/mol)}$	

Table 4.5: Physical and thermodynamic properties of butyl acrylate

Property Expression	Reference
$V_{M,BuA} = 0.9191 - 0.001012(T - 273.15)$	E. Kuindersma (1992)
$V_{P,BuA} = 1.212 - 0.000845(T - 273.15)$	E. Kuindersma (1992)
$Cp_{M,BuA} = 0.430$	E. Kuindersma (1992)
$Cp_{P,BuA} = 0.400$	E. Kuindersma (1992)
$k_{M,BuA} = -1.0845 \times 10^{-2} + 7.1371 \times 10^{-5} T + 1.8829 \times 10^{-8} T^2$	Yaw's Handbook (2005)
$-\Delta H_{BuA} = 18400$	E. Kuindersma (1992)

The weight fraction of monomers and polymers formed at each point in the reactor is calculated by performing mass balances on monomers considering that monomer consumed is converted to polymer, so the amount of polymer formed is obtained by subtracting monomer mass at each point from mass of its mass fed to the reactor up to that point. In case of ethylene-vinyl acetate, the mass of components at any point in each zone is calculated as follows:

Mass of ethylene at each point:

$$m_{\text{ethylene}} = 28C_{01}u_0(1-y_1)A/1000 + 28\bar{M}_E \quad (4.34)$$

Mass of poly-ethylene at each point:

$$m_{\text{poly-ethylene}} = 28C_{01}u_0A/1000 - 28C_{01}u_0(1-y_1)A/1000 \quad (4.35)$$

Mass of vinyl acetate at each point:

$$m_{\text{vinyl acetate}} = 86.09C_{02}u_0(1-y_2)A/1000 + 86.09\bar{M}_{VAc} \quad (4.36)$$

Mass of poly vinyl acetate at each point:

$$m_{\text{poly-ethylene}} = 86.09C_{02}u_0A/1000 - 86.09C_{02}u_0(1-y_2)A/1000 \quad (4.37)$$

Total mass of reaction mixture is equal to summation of mass of monomers fed to reactor:

$$m_0 = m_{\text{ethylene}} + m_{\text{polyethylene}} + m_{\text{vinylacetate}} + m_{\text{polyvinylacetate}} \quad (4.38)$$

Hence, the mass fraction of component i is:

$$x_i = m_i/m_0 \quad (4.39)$$

In equations (4.34) and (4.36), $\bar{M}_i$ refers to the molar flow rate of ethylene and vinyl acetate fed to reactor at the injection point. The injection point equations for copolymerization system were derived as follows.

Total mass balance:

$$u_f \rho_f = u_o \rho_o + \frac{28\bar{M}_E + 86.09\bar{M}_{VAc} + Mw_S \bar{S} + Mw_I \bar{I}}{A} \quad (4.40)$$

Mass balances on components:

$$\text{Total monomer: } u_f [M]_f = u_o [M]_o + \frac{10^3 (\bar{M}_E + \bar{M}_{VAc})}{A} \quad (4.41)$$

Where, $[M] = [M_E] + [M_{VAc}]$ and $[M]_o = (u_o / u_o) C_{M0} (1 - y_{mo})$

Ethylene and vinyl acetate and other reactants concentrations are as follows:

$$\text{Ethylene: } u_f [M_E]_f = u_o [M_E]_o + \frac{10^3 \bar{M}_E}{A} \quad (4.42)$$

$$\text{Vinyl acetate: } u_f [M_{VAc}]_f = u_o [M_{VAc}]_o + \frac{10^3 \bar{M}_{VAc}}{A} \quad (4.43)$$

$$\text{Initiator: } u_f [I]_f = u_o [I]_o + \frac{10^3 \bar{I}}{A}, \quad [I]_o = (u_o / u_o) C_{I0} (1 - y_{I0}) \quad (4.44)$$

$$\text{Solvent: } u_f [S]_f = u_o [S]_o + \frac{10^3 \bar{S}}{A}, \quad [S]_o = (u_o / u_o) C_{S0} (1 - y_{S0}) \quad (4.45)$$

Concentrations of [SCB], [LCB], [Vinyl] and [Vinylidene], ψ_1 , ψ_2 and λ_i , $\tilde{\lambda}_i$, μ_i , $\tilde{\mu}_i$, $\tilde{\mu}_i$ after injection are described as:

$$u_f [X]_f = u_o [X]_o \quad (4.46)$$

Energy balance:

$$C_{pf} T_f = \frac{A \rho_o u_o C_{po} T_o + (28 \bar{M}_E C_{pE} + 86.09 \bar{M}_{VAc} C_{pVAc} + M w_s \bar{S} + M w_I \bar{I}) T}{A \rho_o u_o + 28 \bar{M}_E + 86.09 \bar{M}_{VAc} + M w_s \bar{S} + M w_I \bar{I}} \quad (4.47)$$

For simulation of copolymerization in a multifeed tubular reactor Equations (4.40), (4.41) and (4.47) were simultaneously solved by Gauss-Newton method and subsequently other components concentrations were found using Equations (4.42)-(4.46).

The expressions above remain valid for butyl acrylate except that $M_w=128.17$ g/mol instead of $M_w=86.09$ g/mol.

4.2.3 Molecular properties for copolymerization

The various accumulated molecular properties such as molecular weight averages, comonomer composition, and conversion and the LCB and SCB frequencies can be expressed in terms of the leading moments of chain-length distribution.

Integration of the kinetic model allows the computation of monomer conversion, copolymer composition and molecular weight averages of the polymer as expressed below.

Monomer i accumulated conversion (mol %):

$$y_i = \left(1 - \frac{u[M_i]A/1000}{u_0[M_i]_0 A/1000 + \bar{M}_i} \right) \times 100 \quad (4.48)$$

Calculation of ψ_1 and ψ_2 , the concentration of monomer 1 and 2 bounded in the polymer chains, using Equations (4.43)-(4.44) leads to estimating of polymer accumulated composition $\bar{F}_i$, which is the most important factor affecting the copolymer properties.

The mass fraction of monomer M_i in the copolymer, $\bar{F}_{wi}$ is given by:

$$\bar{F}_{w1} = \frac{\psi_1 M w_1}{\psi_1 M w_1 + \psi_2 M w_2} \quad (4.49)$$

$$\bar{F}_{w2} = 1 - \bar{F}_{w1} \quad (4.50)$$

Number and weight average molecular weights are:

$$\bar{M}_n = M w_{co} \frac{\mu_{1\text{ total}}}{\mu_{0\text{ total}}} = \frac{M w_{co} \{\mu_1 + \tilde{\mu}_1 + \tilde{\tilde{\mu}}_1 + \lambda_1 + \tilde{\lambda}_1\}}{\mu_0 + \tilde{\mu}_0 + \tilde{\tilde{\mu}}_0 + \lambda_0 + \tilde{\lambda}_0} \quad (4.51)$$

$$\bar{M}_w = M w_{co} \frac{\mu_{2\text{ total}}}{\mu_{1\text{ total}}} = \frac{M w_{co} \{\mu_2 + \tilde{\mu}_2 + \tilde{\tilde{\mu}}_2 + \lambda_2 + \tilde{\lambda}_2\}}{\mu_1 + \tilde{\mu}_1 + \tilde{\tilde{\mu}}_1 + \lambda_1 + \tilde{\lambda}_1} \quad (4.52)$$

λ_i , $\tilde{\lambda}_i$, μ_i , $\tilde{\mu}_i$ and $\tilde{\tilde{\mu}}_i$ ($i=0, 1, 2$) are computed using equations (3.21)-(3.34) with rate constants in Table 4.1. In copolymerization, a problem arises from the definition of molecular weight for reactants mixture due to the different molecular weights of comonomers. A general approximation for the molecular weight is:

$$Mw_{co} = Mw_1 \times \bar{F}_1 + Mw_2 \times \bar{F}_2 \quad (4.53)$$

Where $\bar{F}_1$ and $\bar{F}_2$ are the accumulated copolymer compositions for monomer 1 and 2.

4.3 Simulation of ethylene copolymerization in tubular reactor

Simulation results are discussed in order to compare the effect of feeds compositions and monomer types on the properties of the polymer product resulting from free radical copolymerizations of ethylene/vinyl acetate and ethylene/butyl acrylate using difunctional initiators in a high pressure tubular reactor. The tubular reactor consists of two sections based on the number of initiator and monomer injection points. Each reactor section may be divided to a number of reaction and cooling zones. The total flow rate of monomers (ethylene and comonomer) and initiator is split into two feed streams; a front feed stream and a side quenching one. The computer code written in Matlab is capable of taking into account simultaneous injection of both monomers as well as initiator and solvent.

4.3.1 Effect of feed composition on reactor performance and product quality

This section of the simulation starts with analysis of the effect of feed composition on the overall reactor performance and molecular properties of the polymer such as average molecular weights, copolymer composition, and long- and short- chain branching frequencies. The cases studied consisted of copolymerizations of ethylene-butyl acrylate and ethylene-vinyl acetate difunctional initiator using 2,2-bis(tert-butylperoxy)-butane. The comonomer content in feed were 0, 5 and 10 wt%. The operating condition for this simulations were the same as optimum operating conditions of Table 3.7 for difunctional initiator 2,2-bis(tert-butylperoxy)-butane.

Figure 4.1a and 4.1b show temperature profile for ethylene-butyl acrylate and ethylene-vinyl acetate copolymerization runs respectively. The plots show that the reactor temperature is more sensitive to butyl acrylate content than to that of vinyl acetate. Varying butyl acrylate content in the feed from 5 to 10 wt% accelerates reaction and shifts the temperature peak to the left. With butyl acrylate, temperature peak are distinct

and the highest peak corresponds to the highest butyl acrylate content in the feed. Increasing temperature with butyl acrylate content could be related to higher polymerization heat (Equation (4.54)), produced in this reaction as observed in Figure 4.2a.

$$(-\Delta H) = \{(-\Delta H_1)(K_{P11}\varphi_1 + K_{P21}\varphi_2)[M_1] + (-\Delta H_2)(K_{P12}\varphi_1 + K_{P22}\varphi_2)[M_2]\}(\lambda_0 + \tilde{\lambda}_0) \quad (4.54)$$

Obviously, the monomer conversion follows the temperature trend as it is confirmed in figure 4.3a. With vinyl acetate as a comonomer, the temperature profiles are however hampered as the vinyl acetate content increases in the feed. For ethylene-vinyl acetate, heat of reaction is lowered by increasing vinyl acetate content (Figure 4.2b). Besides, plot in Figure 4.1b demonstrates that the first three temperature peaks are not quite distinct from each other. But the monomer conversions overlap as the temperature rises toward peak value at which the monomer conversion settle to different final values (Figure 4.3b). As Figure 4.4a shows, average molecular weight averages boosts as butyl acrylate feed content increases, which could be attributed to increasing rates of termination, transfer to polymer and monomer reactions with increasing butyl acrylate content (Figures 4.5a, 4.6a and 4.7a). However, for ethylene-vinyl acetate, average molecular weight decreases due to reduction of the rate of termination and transfer to polymer (Figure 4.5b and 4.7b).

Degree of branching is an important factor affecting polymer properties. For free-radical copolymerizations such as ethylene-vinyl acetate, ethylene-butyl acrylate, the activation energy for chain branching is greater than that for chain propagation, and branching is expected to increase with temperature. In Figures 4.8-4.9, the plots of long- and short-chain branching per 1000 carbon atoms are depicted with respect to the reactor length. In general, by increasing butyl acrylate and vinyl acetate contents in feed, all those structural properties increased.

The polymerization mechanism of butyl acrylate is greatly influenced by transfer reactions, especially transfer to polymer resulting in long chain branching. It is well known that branching occurs in vinyl acetate as the result of transfer reactions with both monomer and polymer and that the formation of insoluble gel material is observed at high conversions.

In copolymerization of ethylene and butyl acrylate, the acrylate content in the copolymer chains will be higher than feed composition. At high pressure, 2000 bar and 220 °C, Bubak and coworkers (1996) reported the reactivity ratios of ethylene and butyl acrylate as $r_1=0.052$ and $r_2=3.4$. It is apparent that, in copolymerization of ethylene and butyl acrylate, live polymer chains ending in an ethylene radical will favor cross-propagation rather than homopropagation reactions. In contrast, the reactivity ratios for ethylene-vinyl acetate are almost equal resulting in a uniform copolymer composition. This trend could be better observed by plots of copolymer composition for copolymerization of ethylene with butyl acrylate and vinyl acetate as demonstrated in Figure 4.10.

To control copolymer composition, especially when reactivity ratios are much different, it is possible to inject the less reactive monomer in order to reach final desired composition. To find out the effect of injection of monomer on copolymer composition, in Figure 4.11, vinyl acetate was injected ($\bar{M}_i = 2 \text{ kg/s}$) at length $z=0.5$ to the reactor. The front feed composition of vinyl acetate in this simulation was considered $f_{VAc}=22.22 \text{ wt\%}$. The overall copolymer composition in vinyl acetate remains constant along the tube and approximately equal to the initial monomer feed composition ($\bar{F}_{VAc} = 22.97 \text{ (wt\%)}$ at injection point), that is because the reactivity ratios for ethylene and vinyl acetate are approximately the same. Even after vinyl acetate injection, the vinyl acetate composition shifts but still remains constant along the reactor and finally reaches $\bar{F}_{VAc} = 28.22 \text{ (wt\%)}$ at the reactor end.

For ethylene-butyl acrylate simulation, the feed composition was considered $f_{BuA}=5 \text{ (wt \%)}$ and ethylene which is the less reactive component was injected with flow rate ($\bar{M}_i = 1.32 \text{ kg/s}$) to middle of the tube. As stated before, the acrylate content in copolymer is significantly higher than the respective monomer feed, ($\bar{F}_{BuA} = 27.2 \text{ (wt\%)}$ at injection point), because live polymer chains ending in ethylene unit will favor cross-propagation with acrylate monomers. So to control composition ethylene was fed to middle of the reactor and as demonstrated in Figure 4.12, the final butyl acrylate content was reduced to $\bar{F}_{BuA} = 18 \text{ (wt\%)}$.

a)

b)

Figure 4.1: Prediction of temperature Profile for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

Figure 4.2: Prediction of polymerization heat for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

a)

b)

Figure 4.3: Prediction of conversion for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

a)

b)

Figure 4.4: Prediction of average molecular weights for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

a)

b)

Figure 4.5: Prediction of rate of transfer to polymer for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

a)

b)

Figure 4.6: Prediction of rate of transfer to monomer for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

Figure 4.7: Prediction of rate of termination for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

a)

b)

Figure 4.8: Prediction of long chain branching for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

Figure 4.9: Prediction of short chain branching for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

Figure 4.10: Prediction of copolymer composition for a) Ethylene-butyl Acrylate b) Ethylene-vinyl acetate, using 2,2-bis(tert-butylperoxy)-butane.

Figure 4.11: Ethylene-vinyl acetate accumulated copolymer compositions for injection of vinyl acetate .

Figure 4.12: Ethylene-butyl acrylate accumulated copolymer compositions for injection of ethylene.

Chapter 5 Optimization of LDPE reactors

In LDPE industry there is considerable economic incentive to develop real-time optimal policies that can increase production and improve the polymer quality. One of the most crucial problems in the operation of polyethylene reactors is the determination of optimal operating conditions that maximize the reactor productivity for a desired product quality. Steady state models of continuous polymerization reactors are very useful to investigate process behavior for different recipes and operating conditions which yield improved productivity and quality. The goal of this chapter is the development of optimal criteria that can be applied to the operation of high pressure reactors for ethylene polymerization.

5.1 Optimal control objective and decision variables

Polyethylene end-use properties such as density, melt index, impact strength, rigidity and tensile strength, are related to the molecular structure of polymers. The structure of polymer molecules can be described in terms of molecular properties such as molecular weight distribution (MWD), polydispersity index (PDI), degree of branching distribution (DBD), long chain branching (LCB), short chain branching (SCB) and copolymer composition distribution (CCD). Simulation results from previous chapters reveals that for a given reactor configuration, the molecular properties depend strongly on the operating conditions. Therefore, the production of polymers with pre-specified end-use properties are closely related to a good operation of the reactor.

Polymer production and molecular properties of polymer chains depend upon a number of control variables, which are:

- *Initiator and solvent variables*: type and number of initiator and solvent, feed rates and concentrations and number and location of initiator and solvent feed points.
- *Heat transfer variables*: feed temperature, number and length of heating-cooling zones, jacket temperature and the heat transfer coefficient.
- *Reaction variables*: polymerization temperature, pressure, monomer feed concentration and rate, number and location of monomer side feed points and reaction time.

Obviously, the number of possible control variables is very large. Therefore, the selection of control variables is directly related to the specific design of the process, its operational modes and the sensitivity of the reactor behavior to the manipulation of the control variables and the objective function.

Operation of a typical reactor can be optimized in different ways based on the choice of the objective function and control variables. An objective function can be formulated such that the high pressure LDPE reactor operates at the maximum production rate and produces a polymer with desired molecular properties. The objective function is mathematically described as:

$$\text{Maximize: } J = w_1 X_M + w_2 (\bar{M}_n / \bar{M}_{nd} - 1)^2 + w_3 (PDI / PDI_d - 1)^2 + w_4 (\bar{F}_w / \bar{F}_{wd} - 1)^2 \quad (5.1)$$

Subject to:

$$\text{Process model equations} \quad (5.2)$$

$$\text{Control variables constraints } T_{\text{jacket}}, [I]_f, T_{in}, P_{in}, [S]_f, f_{wi}, l_i \quad (5.3)$$

$$\text{Dependent variables bound } T_{\max}(z) \leq 300^\circ\text{C} \quad (5.4)$$

In the right hand side of equation (5.1), the first term represents polymer production, the second and third terms represent the polymer molecular properties and the fourth term represents the copolymer composition.

The objective function J is an implicit function of the control variables. Therefore, the general static optimization problem is to maximize the objective function subject to model equations describing the quantitative relationships between state and control variables and the inequality constraints imposed on the state and control variables.

The optimization problem (5.1) was solved using the sequential quadratic method (SQP) which is a built-in Matlab function. The SQP represents a state-of-the-art in nonlinear programming methods. The SQP implementation consists of three main stages:

- Updating of the Hessian matrix of the Lagrangian function

$$H_{k+1} = H_k + \frac{q_k q_k^T}{q_k^T s_k} - \frac{H_k^T H_k}{s_k^T H_k s_k}$$

$$s_k = x_{k+1} - x_k$$

$$q_k = \nabla f(x_{k+1}) + \sum_{i=1}^n \lambda_i \nabla g_i(x_{k+1}) - \left(\nabla f(x_k) + \sum_{i=1}^n \lambda_i \nabla g_i(x_k) \right)$$

Where $f(x)$ is the function to be minimized and $g(x)$ is the vector of constraints.

Gradient of the Lagrangian function is defined as: $\nabla_x L = \nabla f(x) + \sum_{i=1}^m \lambda_i \nabla g_i(x)$

λ_i is an estimate of the Lagrange multipliers.

- Quadratic programming problem solution to find search direction d

minimize: $\nabla L^T \Delta x + \frac{1}{2} \Delta x^T H \Delta x$

subject to: $\nabla g \Delta x + g = 0, \quad l \leq \bar{x} + \Delta x \leq u$

- Line search and merit function calculation

$x_{k+1} = x_k + \alpha_k d_k$

where d_k is search direction: $d = -H^{-1} \nabla L(x, \lambda)$ and α_k is step length parameter determined in order to produce sufficient decrease in a merit function:

$$\psi(x) = f(x) + \sum r_i g_i(x) + \sum_{i=m_g+1}^m r_i \max\{0, g_i(x)\}$$

At each major iteration, an approximation is made of the Hessian of the Lagrangian function using a Quasi-Newton updating method. This is then used to generate a quadratic programming sub-problem whose solution is used to form a search direction for a line search procedure.

5.2 Tubular reactor optimization

Integration of the model gives the reacting mixture temperature along the axial length, and shows that the process exhibits a maximum temperature $T_{\max}(z)$. The objective function was modified as follows:

$$J = w_1 X_M + w_2 \left(\bar{M}_n / \bar{M}_{nd} - 1 \right)^2 + w_3 \left(PDI / PDI_d - 1 \right)^2 + w_4 \left(\bar{F}_w / \bar{F}_{wd} - 1 \right)^2 + w_5 \text{INT} \left\{ \frac{T_{\max}}{300 + 273.15} \right\} \quad (5.5)$$

With this performance index, the reactor temperature is prevented from going over 300°C. In this thesis, several optimization scenarios were considered for homo- and co-polymerization systems.

5.2.1 Ethylene homopolymerization optimization

For homopolymerization of ethylene in tubular reactor, the control variables considered were initiator and solvent concentrations and jacket average temperatures in each zone. It is known that high initiator concentration increases conversion. However, uncontrolled high concentrations of primary radicals can cause decomposition of ethylene since the reaction is exothermic and possibility of runaway due to a build-up of residue on the reactor wall. Hence, the initiator concentration is an important decision variable affecting the reactor performance.

In the first scenario, optimization of homopolymerization of ethylene was examined. The objective was to maximize productivity while maintaining reactor temperature below 300°C. The average molecular weights or polydispersity were not part of the objective function. So, the weighting factors w_2 , w_3 and w_4 were set to zero. As Matlab optimization functions perform minimization ($\min(J) = -\max(J)$), maximization of conversion is achieved by supplying coefficients $w_1 = -1$ and $w_5 = -100$. Lower and upper bounds placed on each of the decision variables for homopolymerization of ethylene are as follows:

$$110 \leq T_{\text{Jacket}} \leq 270 \text{ } ^\circ\text{C}, \quad 5 \leq [I] \leq 50 \text{ ppm}, \quad 0 \leq [S] \leq 5 \text{ mol/L}$$

Table 5.1 provides the optimal values of the decision variables T_J and $[I]$ in the reactor.

Upon considering plots in Figures 5.1 and 5.2, it is obvious that the optimal case gives higher ethylene conversion (13.35%) even though the corresponding peak temperature is lower than that in the base case. The solid line in Figure 5.1 represents the optimal temperature trend which is optimally computed so that the initiator is not completely depleted; whereas in the base case the reactor temperature rises quickly to over 200°C. The initiator depletes instantaneously and the reaction proceeds with thermal initiation only giving low conversion about 7%.

Optimization results with difunctional peroxides are plotted in Figure 5.3 to 5.8. Both runs generate similar optimal temperature trends with respect to the temperature in the base case. The optimization scheme computes an optimal temperature so that ethylene conversion is maximized along the reactor length. Ethylene conversion profile runs above

that computed in the base case. In the base cases, the peak temperature goes up to over the ceiling temperature (300 °C), thus depleting the initiator and limiting ethylene conversion to about 15.4 % and 15.8 % for peroxide II and III, respectively.

Table 5.1: Reactor performance at optimal operating conditions for Dioctanoyl to maximize conversion.

<i>Dioctanoyl</i>	$T_{1,J}$ (°C)	$T_{2,J}$ (°C)	$T_{3,J}$ (°C)	$[I]$ ppm	PDI	$\bar{M}_n$ (g/mol)	T_{max} (°C)	y_m (%)
Base Case	150	150	90	25	2.67	107080	206.6	6.97
Optimal	107.6	150.02	101.7	27.3	2.94	137940	188.3	13.35

Figure 5.1: Base and optimal temperature profiles using dioctanoyl peroxide to maximize conversion.

Figure 5.2: Effect of optimal policies on maximizing conversion using dioctanoyl peroxide.

Table 5.2: Reactor performance at optimal operating conditions for 2,2-bis(tert-butylperoxy)-butane to maximize conversion.

BU	$T_{1,J}$ (°C)	$T_{2,J}$ (°C)	$T_{3,J}$ (°C)	$[I]$ ppm	PDI	$\bar{M}_n$ (g/mol)	T_{max} (°C)	y_m (%)
Base Case	220	220	180	15	2.927	38020	296.13	15.36
Optimal	223.35	211.65	193.16	14.78	2.88	41950	272.27	19.38

Figure 5.3: Base and optimal temperature profiles using 2,2-bis(tert-butylperoxy)-butane to maximize conversion.

Figure 5.4: Effect of optimal policies on maximizing conversion using 2,2-bis(tert-butylperoxy)-butane.

Table 5.3: Reactor performance at optimal operating conditions for 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate to maximize conversion.

<i>DHBPPI</i>	$T_{1,j}$ (°C)	$T_{2,j}$ (°C)	$T_{3,j}$ (°C)	$[I]$ ppm	<i>PDI</i>	$\bar{M}_n$ (g/mol)	T_{max} (°C)	y_m (%)
Base Case	225	225	180	10	3.0866	33580	312.8	15.82
Optimal	232.9	209.45	185.36	10.41	3.1	37270	284.72	22.87

Figure 5.5: Base and optimal temperature profiles using 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate to maximize conversion.

Figure 5.6: Effect of optimal policies on maximizing conversion using 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate.

In the second run, the number average molecular weight $\bar{M}_n$ is constrained to lie at a desired value of $\bar{M}_{nd} = 21900$. The two constraints on reactor temperature and number average molecular weight are handled as penalty functions. The weighting factors assigned to the objective function are: $w_1 = -1$, $w_2 = -100$, $w_3 = 0$, $w_4 = 0$ and $w_5 = -100$. The decision variables are jacket temperatures and initiator and solvent concentrations. Conversion and reaction peak temperature are controlled by manipulating initiator concentration and jacket temperature and the number average molecular weight is expected to decrease by increasing solvent concentration in feed. The operating conditions and dependant variables in base and optimal cases are reported in table 5.4. It is observed from Figures 5-7- 5.9 that by increasing solvent concentration, $\bar{M}_n$ is reduced to desired value, however conversion slightly decreased.

Table 5.4: Reactor performance at optimal operating conditions for 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{M}_{nd} = 21900$.

<i>BU</i>	$T_{1,J}$ (°C)	$T_{2,J,J}$ (°C)	$T_{3,J}$ (°C)	$T_{4,J}$ (°C)	$T_{5,J}$ (°C)	$[I]$ ppm	$[S]$ mol/L
Base Case	220	220	220	180	180	20	0.0041
Optimal	213.2	223.9	219.4	180	179	12.67	0.0298

<i>BU</i>	PDI	$\bar{M}_n$	T_{max}	y_m (%)
Base Case	2.8908	32900	299.1	15.42
Optimal	2.5222	23090	287.8	14.976

Figure 5.7: Base and optimal temperature profiles using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{M}_{nd} = 21900$.

Figure 5.8: Effect of optimal policies on maximizing conversion using 2,2-bis(tert-butylperoxy)-butane with $\bar{M}_{nd} = 21900$.

Figure 5.9: Effect of optimal policies on average molecular weight using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{M}_{nd} = 21900$.

5.2.2 Ethylene copolymerization optimization

As it was pointed out in Chapter 4, controlling copolymer composition is very important because it influences end-use properties of the copolymer. Also, the comonomer content affects the reactor peak temperature. Besides jacket temperature and initiator concentrations, feed composition and inlet feed flow rate were manipulated as control variables.

Ethylene/Butyl Acrylate copolymerization optimization

The objective function is to maximize conversion and get copolymer with a butyl acrylate content of 12 wt%. As it was concluded from simulation results of Chapter 4, because of the higher reactivity ratio of butyl acrylate in comparison with ethylene, its composition in polymer is higher than feed, so to reach a desired copolymer composition one should decide on selecting butyl acrylate feed content. For this optimization problem, the desired copolymer composition was $\bar{F}_{BuA,d} = 12(\text{wt}\%)$. The optimal operating conditions and molecular properties of copolymer resulting from optimization are in table 5.5 and Figures 5.10-5.12.

Table 5.5: Reactor performance at optimal operating conditions for ethylene/butyl acrylate using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{BuA,d} = 12(\text{wt}\%)$.

<i>BU</i>	$T_{1,j} (^{\circ}\text{C})$	$T_{2,j} (^{\circ}\text{C})$	$T_{3,j} (^{\circ}\text{C})$	$F_{BuA}(\text{wt } \%)$	$F_{in}(\text{kg/s})$	$[I], \text{ppm}$	$[S], \text{mol/L}$
Base Case	200	200	180	5	10.45	20	0
Optimal	218.45	205.27	193.26	2.98	11.72	20.6	5×10^{-4}

<i>BU</i>	$y_m(\%)$	$\bar{F}_{BuA}(\text{wt}\%)$	<i>PDI</i>	$\bar{M}_n$	$T_{max} (^{\circ}\text{C})$
Base Case	6.41	36.95	2.2124	102410	217.1
Optimal	22.87	11.99	2.93	48490	272.15

Figure 5.10: Base and optimal temperature profiles for ethylene/butyl acrylate copolymerization using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{\text{BuA,d}} = 12(\text{wt}\%)$.

Figure 5.11: Effect of optimal policies on maximizing conversion ethylene/butyl acrylate copolymerization using 2,2-bis(tert-butylperoxy)-butane with $\bar{F}_{\text{BuA,d}} = 12(\text{wt}\%)$.

Figure 5.12: Effect of optimal policies on copolymer composition for ethylene/butyl acrylate copolymerization using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{BuA,d} = 12(\text{wt}\%)$.

Ethylene/Vinyl acetate copolymerization optimization

In this run, similar to the previous case objective was to maximize conversion while getting a vinyl acetate content of $\bar{F}_{VAc,d} = 12(\text{wt}\%)$ in copolymer. The decision variables were jacket temperature, initiator and solvent concentrations as well as feed composition. As it was expected and observed from Figure 5.15, due to similar reactivity ratios of ethylene-vinyl acetate the optimization procedure reduced the feed composition almost equal to final desired copolymer composition. This result proves that the procedure work properly and was able to predict the optimal policies correctly.

Table 5.6: Reactor performance at optimal operating conditions for ethylene/vinyl acetate using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{VAc,d} = 12(\text{wt}\%)$.

<i>BU</i>	$T_{1,J} (^{\circ}\text{C})$	$T_{2,J} (^{\circ}\text{C})$	$T_3 (^{\circ}\text{C})$	$F_{VAc}(\text{wt} \%)$	$F_{in}(\text{kg/s})$	$[I], \text{ppm}$	$[S], \text{mol/L}$
Base Case	200	200	180	20	8.8	20	0
Optimal	230.6	203.31	224.5787	11.52	10.0837	11.83	0

<i>BU</i>	$y_m(\%)$	$\bar{F}_{VAc}(\text{wt}\%)$	<i>PDI</i>	$\bar{M}_n$	$T_{max} (^{\circ}\text{C})$
Base Case	3.45	20.76	3.1147	29860	208
Optimal	21.23	11.99	3.25	27390	269.53

Figure 5.13: Base and optimal temperature profiles for ethylene/vinyl acetate copolymerization using 2,2-bis(tert-butylperoxy)-butane to maximize conversion with $\bar{F}_{VAc,d} = 12(\text{wt}\%)$.

Figure 5.14: Effect of optimal policies on maximizing conversion for ethylene/vinyl acetate copolymerization using 2,2-bis(tert-butylperoxy)-butane with $\bar{F}_{VAc,d} = 12$ (wt%) .

Figure 5.15: Effect of optimal policies on maximizing conversion for ethylene/vinyl acetate copolymerization using 2,2-bis(tert-butylperoxy)-butane with $\bar{F}_{VAc,d} = 12$ (wt%) .

Chapter 6 Conclusions and Recommendations

6.1 Conclusions

This study proposed a new kinetic model for high pressure homo- and co-polymerization of LDPE using difunctional initiators in a tubular reactor. Kinetic mechanisms describe the polymerization rate, monomer consumption, polymer production, molecular weight distributions, branching frequencies and copolymer composition. Thermodynamic and transport properties of LDPE (co-)polymerization process were also accounted for in the model development. A computer code was written to simulate the dynamics of an isothermal autoclave reactor and the behavior of steady state non-isothermal tubular reactor with multiple feed. The CSTR kinetic model was validated using data collected from for one monofunctional and two difunctional initiators.

The thesis investigates the influence of the initiator type and reaction temperature on conversion and molecular averages in both reactor systems. The CSTR model and data demonstrated that ethylene conversion versus temperature goes through a maximum value. It was observed that ethylene conversion using a difunctional peroxide is twice that obtained with a dioctanoyl peroxide, even though the initial concentration of the later peroxide was four times higher.

Polymer produced using difunctional initiator has higher polydispersity and wider molecular weight distribution which can be attributed to increased degree of branching due to difunctionality of the peroxides. The tubular reactor performance is significantly influenced by the type of initiator and location of initiator and monomer injection points. The simulation revealed that the jacket temperature is a key variable to monitor the reactor temperature and hence prevents a process runaway.

For copolymerization, ethylene-vinyl acetate and ethylene-butyl acrylate systems were studied. The effect of multiple feed on the performance of tubular reactor was investigated for polymerization of LDPE and it was concluded that upon splitting the feed conversion boosts and better temperature control due to quenching of the reactor contents would be obtained. However, the structural properties of the produced polymer such as long- and short- chain branching and double groups also increase. It was

observed that for copolymerization when the reactivity ratios are much different copolymer composition could be controlled by injecting the less reactive monomer.

The optimization of LDPE copolymerization in non-isothermal tubular reactor was also conducted in this study. The optimization scheme computed temperature profile to maximize monomer conversions with desired final product quality in terms of average molecular weights and copolymer composition. The reactor temperature profile was optimally computed so that the initiator is moderately consumed and the reactor temperature remains well below the ceiling temperature.

6.2 Recommendations

- Extending the work to dynamic modeling of LDPE process using difunctional initiators and applying dynamic optimization policies to determine start-up/shut-down strategies to minimize the transient states generated during the switching between different steady states.
- Applying multi-objective optimization methods to resolve the limitations resulting from scalarization of the objective function in order to enable decision maker to select best policy using pareto-optimal solutions.
- If possible, setting up pilot-plant LDPE polymerization reactors and performing lab-scale experiments in order to investigate the accuracy of simulation results with data for difunctional initiators.

References

- Agrawal N., G. P. Rangaiah, A. K. Ray and S. K. Gupta, "multi-objective optimization of the operation of an industrial low-density polyethylene tubular reactor using genetic algorithm and its jumping gene adaptation", *Industrial and Engineering Chemistry Research*, 45(9), 3182-3199 (2006).
- Agrawal, S. C. and C. D. Han, "Analysis of the high-pressure polyethylene tubular reactor with axial mixing", *AIChE*, 21(3), 449-465 (1975).
- Albert J. and G. Luft, "Thermal decomposition of ethylene-comonomer mixtures under high pressure", *AIChE*, 45 (10), 2214-2222 (1999).
- Asteasuain M., S. M. Tonelli, A. Brandolin and J. A. Bandoni, "Dynamic simulation and optimization of tubular polymerization reactors in gPROMS", *Computers and Chemical Engineering*, 25(4), 509-515 (2001).
- Baltsas, A., E. Papadopoulos and C. Kiparissides, "Application and validation of the pseudo-kinetic rate constant method to high pressure LDPE Tubular reactors" *Computers and Chemical Engineering*, 22(suppl.), S95-S102 (1998).
- Becker P., M. Busch, "Modeling of ethylene copolymerization with acrylate monomers", *Macromol. Theory Simul*, 7, 435 (1998).
- Beuermann S., M. Buback, D. Nelke, "Pressure dependence of the propagation rate coefficient k_p for vinyl acetate polymerizations in bulk and in solution of fluid CO_2 ", *Macromolecules* 34, 6637 (2001)
- Boxtel, M. H. C. and M. Busch, "A general model describing molecular weight distribution and branching indices in copolymerizations demonstrated by the high

pressure free radical copolymerization of ethane and methyl acrylate”, *Macromolecular Theory and Simulations*, 10(1), 25-37 (2001).

Brandolin A., E. M. Valles and J. N. Farber, ”High pressure tubular reactors for ethylene polymerization optimization aspects”, *Polymer engineering and science*, 31(5), 381-390, (1991).

Brandolin A., M. H. Lacunza, P. E. Ugrin, and N. J. Capiati, ”High pressure polymerisation of ethylene. An improved mathematical model for industrial tubular reactors”, *Polymer Reaction Engineering*, 4(4), 193-241 (1996).

Brandolin A., N. J. Capiati., J. N. Farber, and E. M. Valles, ”Mathematical model for high-pressure tubular reactor for ethylene polymerisation”, *Industrial and Engineering Chemistry Research*, 27(5), 784-790 (1988).

Brandrup J., H. Immergut, Edmund, Eric A. Grulke, A. Akihiro and D. R. Bloch, *Polymer Handbook* (4th Edition), 2005 John Wiley & Sons.

Brown F. E. and G. E. Ham, ”General conclusions about the copolymerization of ethylene with other monomers by free radical catalysis”, *Journal of Polymer Science Part A: General Papers* , 2(8), 3623 – 3632 (1964).

Buback M., M. Bush, K. Lovis and F. Mahling, ”High-pressure free-radical copolymerization of ethane and Butyl acrylate”, *Macromolecular Chemistry and Physics*, 197, 303-313 (1996).

Burkhart R. D. and N. L. Zutty, ”Copolymerization studies. III. Reactivity ratios of model ethylene copolymerizations and their use in $Q-e$ calculations”, *Journal of Polymer Science Part A: General Papers*, 1(4), 1137-1145 (1963).

Cervantes A., S. Tonelli, A. Brandolin, A. Bandoni and L. Beigler, "Large-scale dynamic optimization of a low-density polyethylene plant", *Computers and Chemical Engineering*, 24, 983-989 (2000).

Chen C. H., J. G. Vermeychuk, J. A. Howell and P. Ehrlich, "Computer model for tubular high-pressure polyethylene reactors", *AIChE*, 22 (3), 463-471 (1976).

Choi K. Y. and G. D. Lei, "Modeling of free radical polymerization of styrene by bifunctional initiators", *AIChE Journal*, 33(12), 2067-2076 (1987).

Choi K. Y., G. D., Lei and W. R. Liang, "Kinetic bulk styrene polymerization catalyzed by symmetrical bifunctional initiators", *Journal of Applied Polymer Science*, 35, 1547-1562 (1988).

Dhib R., J. Gao and A. Penlidis, "Simulation of free radical bulk/solution homopolymerization using mono- and bi-functional initiators", *Polymer Reaction Engineering*, 8(4), 299-464 (2000).

Dhib R. and N. Al-Nidawy, "Modeling of free radical polymerization of ethylene using difunctional initiators", *Chemical Engineering Science*, 57, 2735-2746 (2002)

Donati G., L. Marini, G. Marziano, C. Mozafferi, M. Spampinato and E. Langianni, "Mathematical model of low-density polyethylene tubular reactors", *Chemical Reaction Engineering*, Wei, J. Georgakis, C. (Eds), American Chemical Society Symposium Series 196, American Chemical Society: Washington, DC, 579-590 (1982).

Feucht P., B. Tilger and G. Luft, "Prediction of molar mass distribution, number and weight average degree of polymerisation and branching of low density polyethylene", *Chemical Engineering Science*, 40 (10), 1935-1942(1985).

Friis N. and A. E. Hamielec, "Kinetic of vinyl chloride and vinyl acetate emulsion polymerization", J. of Applied Polymer Science, 19, 97 (1975).

Ghiass M. and R. A. Hutchinson, "Simulation free-radical high-pressure copolymerization in a multizone autoclave: Model development and application", Polymer Reaction Engineering, 11(4), 989-1015 (2003).

Ghiass M. and R. A. Hutchinson, "Simulation of free-radical high-pressure copolymerization in a multizone autoclave: Compartment model investigation", Macromolecular. Symposium, 206,443-456 (2004).

Gloor P. E., A. E. Hamielec and W. Chan., "Kinetic model for olefin polymerization in high-pressure autoclave reactors", AIChE Journal, 39(1), 111-126 (1993).

Goto S., K. Yamamoto, S. Furui and M. Sugimoto, "Computer Model for commercial high pressure polyethylene reactor based on elementary reaction rates obtained experimentally", J. Applied Polymer Science: Applied Polymer Symposium, 36, 21-40. (1981).

Gupta S. K., A. Kumar and M. V. G. Krishnamurthy, "Simulation of tubular low density polyethylene", Polymer Engineering and Science, 25(1), 37-47 (1985).

Ham J. Y. and H. K. Rhee, "Modelling and control of an LDPE autoclave reactor", Journal of Process Control, 6(4), 241-246 (1996).

Hamer J. W. and W. H. Ray, "Continuous tubular polymerization reactors-I :A detailed model", Chemical Engineering Science, 41(12), 3083-3093 (1986)

Hulburt, H. M., and S.Katz, "Some Problems in Particle Technology; A Statistical Mechanical Formulation", Chemical Engineering Science. 19,555 (1964).

- Kalyon D. M., Y.N. Chiou, S. Kovenklioglu and A. Bouaffar, "High-pressure polymerization of ethylene and rheological behaviour of polyethylene product", *Polymer Engineering and Science*, 33, 804 (1994).
- Keramopoulos, A. and C. Kiparissides, "Mathematical modeling of diffusion-controlled free-radical terpolymerization reactions", *J. of Applied Polymer Science*, 88, 161-176 (2003).
- Kim K. J., W. R. Liang and K. Y. Choi, "Bulk free radical polymerization of styrene with unsymmetrical bifunctional initiators", *Industrial and Engineering Chemistry Research*, 28, 131-138 (1989).
- Kiparissides, C and G. Verros, "A comprehensive mathematical model for a multizone tubular high pressure LDPE reactor", *Chemical Engineering Communications*, 121, 193-217 (1993).
- Kiparissides C., G. Verros and J. F. MacGregor, "Mathematical modeling, optimization and quality control of high-pressure Ethylene polymerization reactors", *J.M.S- Rev. Macromol. Chem. Phys.*, C33(4), 437-527 (1993.)
- Kiparissides C., A. Baltsas and S. Apadopoulos, "Mathematical modeling of free-radical copolymerization in high-pressure tubular reactors", *Ind. Eng. Chem. Res.*, 44(8), 2592-2605 (2005).
- Konstadinidis K., D. S. Achilian and C. Kiparissides, "Development of unified mathematical framework for modeling molecular and structural changes in free radical homopolymerization reactions", *Polymer*, 33(23), 5019-5030 (1992).
- Kuindersma M. E., "On the modelling of free-radical polymerization reactions : homopolymerization", M.Sc Thesis, University of Waterloo, Dept. of Chemical Engineering (1992).

Lacunza M. H., M. Asteasuain, P. E. Ugrin and A. Brandolin, "Effect of multiple feedings in the operation of a high-pressure polymerization reactor for ethylene polymerization", *Polymer Reaction Engineering*, 9(3), 163-182 (2001).

Luft G., H. Bitsch and H. Seidl, "Effectiveness of organic peroxide initiators in the high-pressure polymerisation of ethylene", *J. Macromol. Sci.-Chem.*, A11(6), 1089-1112 (1977).

Luft, G. and M. Dorn, "Asymmetrical bifunctional organic peroxides as initiators for the high-pressure polymerisation of ethylene", *J. Macromol. Sci.-Chem.*, A25 (8), 987-998 (1988).

Luft, G., P. Lim, S. Pavlaskis and H. Seidl, "The decomposition of 2,2-Bis(t-butylperoxide)butane under high pressure", *J. Macromol. Sci.-Chem.*, A22(9), 1183-1200 (1985a).

Luft, G. and H. Seidl, "Application of bifunctional organic peroxides in the polymerisation of ethylene under high pressures." *Die Angewandte Makromolekulare Chemie*, 129, 61-70 (1985b).

Marini L. and C. Georgakis, "Low density polyethylene vessel reactors. Part II: A novel controller", *AIChE*, 30(3), 409-415 (1984).

Mavridis, H. and C. Kiparissides, "Optimization of a high-pressure polymerization tubular reactor", *Polymer process engineering* 3(3), 263-290 (1985).

Meyer T. and J. Keurentjes, "Handbook of Polymer Reaction Engineering", Wiley-VCH (2005).

- Poling, B. E., J. M. Prausnitz and J. P. O'Connell, "The properties of gases and Liquids", 5th edition, McGraw-Hill: New York, (2001).
- Prisyazhnyuk, A. I. and S. S. Ivanchev, "Diperoxides with differing thermal stabilities of the peroxide group as initiators of radical polymerization and block copolymerization", Polymer Science USSR 12(2), 514-524 (1970).
- Reid R. C., J. M. Prausnitz and T. K. Sherwood, "The properties of gases and liquids", McGraw-Hill: New York, (1977).
- Scorah, M. J., R. Dhib and A. Penlidis, "Free-radical polymerization of methyl methacrylate with a tetrafunctional peroxide initiator", Journal of Polymer Science, Part A: Polymer Chemistry, 42(22), 5647-5661 (2004).
- Scorah, M. J., R. Dhib and A. Penlidis, "Use of a novel tetrafunctional initiator in the free radical homo- and copolymerization of styrene, methyl methacrylate and α -methyl styrene", Journal of Macromolecular Science -Pure and Applied Chemistry, 42 A(4), 403-426 (2005).
- Scorah, M. J., R. Dhib and A. Penlidis, " Modeling of free radical polymerization of styrene and methyl methacrylate by a tetrafunctional initiator" Chemical Engineering Science, 61(15), 4827-4859 (2006).
- Teymour F. and W. H. Ray, "The dynamic behavior of continuous solution polymerization reactors", Chemical Engineering Science, 44(9), 1967-1982 (1989a).
- Teymour F. and W. H. Ray, "The dynamic behavior of continuous solution polymerization reactors-IV. Dynamic stability and bifurcation analysis of an experimental reactor", Chemical Engineering and Science, 44 (9), 1967-1982 (1989b).

Villalobos M. A., "Synthesis and modeling of high Tg copolymers through suspension copolymerization with bifunctional initiators", Ph.D. Thesis, MacMaster University, Canada, (1994).

Villalobos M. A., A. E. Hamielec and P.E. Wood, "Kinetic model for short-cycle bulk styrene polymerization through bifunctional initiators", Journal of Applied Polymer Science, 42, 629-641 (1991).

Xie T. Y. and A. E. Hamielec, "Modeling free-radical copolymerization kinetics – evaluation of the pseudo-kinetic rate constant method 1: Molecular weight calculations for linear copolymers", Makromol. Chem., Theory Simul. 2, 421-454 (1993a).

Xie T. Y. and A. E. Hamielec, "Modeling free-radical copolymerization kinetics – evaluation of the pseudo-kinetic rate constant method 2: Molecular weight calculations for copolymers with long chain branching", Makromol. Chem., Theory Simul. 2, 455-483 (1993b).

Yao F. Z., A. Lohi, S. R. Upreti and R. Dhib, "Modeling, simulation and optimal control of ethylene polymerization in non-isothermal, high pressure tubular reactors", International Journal of chemical reaction engineering, 2, 1-25 (2004).

Yaws C., "Yaws' Handbook of thermodynamic and physical properties of chemical compounds", Knovel (2003).

Yoon B. J. and H. Rhee, "A study of high pressure polyethylene tubular reactor", Chemical engineering communications, 34, 253-267 (1985).

Yoon W. J. and K. Y. Choi, "Polymerization of styrene in a continuous filled tubular reactor", Polymer Engineering and Science, 36(1), 65-77 (1996)

Zabinsky R. C. M., W. M. Chan, P. E. Gloor and A. E. Hamielec, "A Kinetic model for olefin polymerization in high-pressure tubular reactors: a review and update", *Polymer*, 33(11), 2243-2262 (1992).

Zimmermann H. and T. Pollok, "Advances in organic peroxides for low density polyethylene", *Plastics, Rubber and Composites Processing and Applications*, 27(1), 12-18 (1998).

APPENDIX A. Organic Peroxides

Organic peroxides have long established their position as free-radical initiators in manufacturing of low density polyethylene (LDPE). Though applied in relatively small quantities, they play a crucial role in determining the progress of the reaction and influencing the properties of the polymer. Monofunctional peroxide, dioctanoyl have one oxygen–oxygen bond separating two identical or different organic groups. However, the presence of two or more oxygen–oxygen bonds in di-functional peroxides, 2,2-bis(tert-butylperoxy)-butane and 2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate, makes their kinetic decomposition into radical fragments quite particular. Under the effect of heat, the oxygen bond breaks up, giving rise to two possible free radicals. Various types of macromolecular species, carrying undecomposed functional groups are formed, which upon a subsequent decomposition, will be involved again in the reaction repeatedly through re-initiation, propagation and termination. The chemical structures of initiators used in this study are shown below:

Dioctanoyl Peroxide

2,2-bis(tert-butylperoxy)-butane

(A.3)

2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate

APPENDIX B Initiators efficiency

Dhib and Al-Nidawy (2002), calculated the optimal values of efficiency by fitting data to initiators concentrations and found that the efficiency decreased linearly with initial peroxide concentration regardless of the initiator type. Kim et al. (1989) reported similar observation. In this study, initiators efficiencies were found using linear regression of efficiency data corresponding to Figure B.1.

Figure B. 1: Initiator efficiency ($f_1=f_2$) versus initial initiator concentration

APPENDIX C Reactions with internal radical centers

An internal radical centre is a radical located on a backbone carbon atom and is formed by three reactions: (i) transfer to polymer (ii) Terminal double bond reactions and (iii) backbiting. These internal radical centers can undergo all reactions that chain-end radicals do and propagate leading to branching. The transfer to polymer leads to long chain branches (LCB). This reaction involves the transfer of reactivity from radical type j to a monomertype i mer unit in a dead polymer chain to form a radical with the active centre somewhere along the chain. In presence of monomer, propagation leads to long chain branching:

Where R' denotes an internal radical. And then propagation occurs:

Figure C.1: Formation of long chain branching via transfer to polymer

The reactions of termination by disproportionation, β -scission and transfer to monomer produce chain ends that have double bonds. These double bonds might react with radicals, via a propagation-type reaction, producing internal radicals that can propagate to form long chain branches:

since for the type of polymerization being considered, the conversion of monomer is usually low, the concentration of these terminal double bonds is quite small and for this reason these terminal double bond reactions may be neglected. Backbiting leads to short chain branching (SCB). For the formation of short chain branches via backbiting, the radical activity is transferred to a site along the same chain, and this site may propagate leaving a short chain branch:

and then the propagation:

Figure C.2: Formation of short chain branching via backbiting

Writing a balance on the internal radical types formed by transfer to polymer of chain length r , gives the following relation for long chain branch radicals.

$$\begin{aligned} \frac{d([R_{r(LCB)}^{**}])}{dt} = & [k_{tp11}[sP_s]F_1\phi_1 + k_{tp21}[sP_s]F_1\phi_2 + k_{tp12}[sP_s]F_2\phi_1 + k_{tp22}[sP_s]F_2\phi_2] \lambda_0 \\ & + [k_{tp11}[s\tilde{P}_s]F_1\phi_1 + k_{tp21}[s\tilde{P}_s]F_1\phi_2 + k_{tp12}[s\tilde{P}_s]F_2\phi_1 + k_{tp22}[s\tilde{P}_s]F_2\phi_2] \tilde{\lambda}_0 \\ & - (k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])[R_{r(LCB)}^{**}] \end{aligned} \quad (C.1)$$

Similarly for Live macromolecular radicals of length r carrying un-decomposed peroxide group a balance on the internal radical could be written as:

$$\begin{aligned} \frac{d(\tilde{R}_{r(LCB)}^{**})}{dt} = & [k_{tp11}[sP_s]F_1\phi_1 + k_{tp21}[sP_s]F_1\phi_2 + k_{tp12}[sP_s]F_2\phi_1 + k_{tp22}[sP_s]F_2\phi_2] \tilde{\lambda}_0 \\ & + [k_{tp11}[s\tilde{P}_s]F_1\phi_1 + k_{tp21}[s\tilde{P}_s]F_1\phi_2 + k_{tp12}[s\tilde{P}_s]F_2\phi_1 + k_{tp22}[s\tilde{P}_s]F_2\phi_2] \tilde{\lambda}_0 \\ & - (k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])[\tilde{R}_{r(LCB)}^{**}] \end{aligned} \quad (C.2)$$

Rate of change of concentration of long chain branches is simplified by application of pseudo-kinetic rate constant for transfer to polymer previously stated in Table 4.1:

$$\frac{d([R_{r(LCB)}^{**}])}{dt} = k_{tp}[sP_s]\lambda_0 + k_{tp}[s\tilde{P}_s]\tilde{\lambda}_0 - (k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])[R_{r(LCB)}^{**}] \quad (C.3)$$

$$\frac{d(\tilde{R}_{r(LCB)}^{**})}{dt} = k_{tp}[sP_s]\tilde{\lambda}_0 + k_{tp}[s\tilde{P}_s]\tilde{\lambda}_0 - (k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])[\tilde{R}_{r(LCB)}^{**}] \quad (C.4)$$

Making the stationary-state hypothesis for these internal radicals, expressions for the concentrations of these internal radicals follows:

$$[R_{r(LCB)}^{**}] = \frac{k_{tp}\lambda_0([sP_s] + [s\tilde{P}_s])}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} \quad (C.5)$$

$$[\tilde{R}_{r(LCB)}^{**}] = \frac{k_{tp}\tilde{\lambda}_0([sP_s] + [s\tilde{P}_s])}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} \quad (C.6)$$

And total concentrations of internal radicals are obtained by summation over all polymer radical chain:

$$[R'_{LCB}] = \frac{k_{tp}\lambda_0(\mu_1 + \tilde{\mu}_1)}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} \quad (C.7)$$

$$[\tilde{R}'_{LCB}] = \frac{k_{tp}\tilde{\lambda}_0(\mu_1 + \tilde{\mu}_1)}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} \quad (C.8)$$

Considering the generation of long chain branches, the total number of long chain branching produced is given by:

$$\begin{aligned} \frac{d(C_{LCB})}{dt} &= k_p[M][R'_{LCB}] - (C_{LCB})Q_f \\ &= k_p[M] \times \frac{k_{tp}\lambda_0(\mu_1 + \tilde{\mu}_1)}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} - (C_{LCB})Q_f \\ &= k_{LCB}\lambda_0(\mu_1 + \tilde{\mu}_1) - (C_{LCB})Q_f \end{aligned} \quad (C.9)$$

$$\begin{aligned} \frac{d(\tilde{C}_{LCB})}{dt} &= k_p[M][\tilde{R}'_{LCB}] - (\tilde{C}_{LCB})Q_f \\ &= k_p[M] \times \frac{k_{tp}\tilde{\lambda}_0(\mu_1 + \tilde{\mu}_1)}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} - (\tilde{C}_{LCB})Q_f \\ &= k_{LCB}\tilde{\lambda}_0(\mu_1 + \tilde{\mu}_1) - (\tilde{C}_{LCB})Q_f \end{aligned} \quad (C.10)$$

$$\text{Where } k_{LCB} = k_p[M] \times \frac{k_{tp}}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} \quad (C.11)$$

Similarly, writing a balances on the internal radical types formed by backbiting, gives the following relation for short chain branch radicals.

$$\frac{d([R_{r(SCB)}^{\bullet}])}{dt} = (k_{b1}R_1^{\bullet} + k_{b2}R_2^{\bullet}) - (k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])[R_{r(SCB)}^{\bullet}] \quad (C.12)$$

$$\frac{d([\tilde{R}_{r(SCB)}^{\bullet}])}{dt} = (k_{b1}\tilde{R}_1^{\bullet} + k_{b2}\tilde{R}_2^{\bullet}) - (k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])[\tilde{R}_{r(SCB)}^{\bullet}] \quad (C.13)$$

$$\frac{d\left(\left[\sum_{r=1}^{\infty} R_{r,S}^{\bullet}\right]\right)}{dt} = (k_{b1}\varphi_1 + k_{b2}\varphi_2)\lambda_0 - (k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])[R'_{SCB}] \quad (C.14)$$

$$\frac{d\left(\left[\sum_{r=1}^{\infty} \tilde{R}'_{r,S}\right]\right)}{dt} = (k_{b1}\varphi_1 + k_{b2}\varphi_2) \tilde{\lambda}_0 - (k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S]) [\tilde{R}'_{SCB}] \quad (C.15)$$

$$[R'_{r(SCB)}] = \frac{(k_{b1}\varphi_1 + k_{b2}\varphi_2) \lambda_0}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} \quad (C.16)$$

$$[\tilde{R}'_{r(SCB)}] = \frac{(k_{b1}\varphi_1 + k_{b2}\varphi_2) \tilde{\lambda}_0}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} \quad (C.17)$$

$$\frac{d(C_{SCB})}{dt} = k_p[M] \frac{(k_{b1}\varphi_1 + k_{b2}\varphi_2) \lambda_0}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} - (C_{SCB}) Q_f \quad (C.18)$$

$$\frac{d(\tilde{C}_{SCB})}{dt} = k_p[M] \frac{(k_{b1}\varphi_1 + k_{b2}\varphi_2) \tilde{\lambda}_0}{(k_p[M] + k'_\beta + k_{ym}[M] + k_{ts}[S])} - (\tilde{C}_{SCB}) Q_f \quad (C.19)$$

The expressions derived above permit the calculation of the branching frequencies. Consequently, it will be possible to control some of the polymer physical properties such as density and rheological properties such as melt flow through variation in operating conditions of the reactor.