Model Development and Parameter Estimation for Styrene Polymerization

by John Daniel Woloszyn

A thesis submitted to the Department of Chemical Engineering in conformity with the requirements for the degree of Master of Applied Science

> Queen's University Kingston, Ontario, Canada February, 2012

Copyright © John Daniel Woloszyn, 2012

Abstract

A model is developed to describe the bulk thermally-initiated free-radical polymerization of styrene between 100 °C and 170 °C. This model incorporates a comprehensive thermal initiation mechanism including generation and consumption of a Diels-Alder adduct intermediate species. A semi-empirical break-point treatment of diffusion control on reaction kinetics is used to account for autoacceleration behaviour. Using recently-developed statistical techniques, parameters are ranked based on their influence on model predictions, uncertainty in their initial values and correlation between their effects. The four top-ranked parameters (of the 40 total model parameters) are chosen for estimation to improve the fit between model predictions and literature data. After estimation of these four parameters, and hand-tuning of two additional autoacceleration parameters, the model predicts conversion data with a standard error of 5 %. The model also provides an excellent fit to a single MWD curve obtained from a literature experiment performed at 100 °C. Simulations are used to show that chain-end degradation reactions are not important in the temperature range of interest.

The model is then extended to include industrially-relevant dicumyl peroxide and biphenyl peroxide chemical initiation. Additional peroxide-induced mid-chain scission reactions are considered as they may have an important influence on the molecular weight of polystyrene. To improve trends in predictions of M_n and M_w , the stationary-state hypothesis is applied to the initial adduct concentration. Parameters are then ranked, and selected for estimation using recently-developed statistical techniques. While significant

improvements in predictions of conversion data are obtained, it is necessary to manually tune several parameters and scrutinize the reaction scheme in detail. To improve trends in predictions of M_n and M_w , mid-chain scission reactions are turned off and chain-transfer to monomer is implemented. Nine of the 48 total parameters are selected for estimation, resulting in a 73 % decrease in the objective function value compared with predictions using literature values. The final step of this work will be to estimate parameters using a large, proprietary industrial data set. Using this data set, it may be possible to estimate additional parameters which may lead to improved model predictions.

Acknowledgments

Projects of this magnitude are rarely accomplished in isolation, and my work is no exception. I would like to acknowledge the following people for their aid and support, without which this project would not have been possible.

Dr. Kimberly McAuley, my devoted supervisor, who thoroughly deserves every award and accolade laid upon her for commitment to her students. Thank you for the opportunity to expand my knowledge and skills. I very much enjoyed working with you, and hope to be able to do so again in the future.

This project was sponsored by BASF, who provided valuable insight and support throughout my Master's research. In particular, I would like to acknowledge Dr. Klaus-Dieter Hungenberg, Dr. Thomas Bott, Dr. Pascal Hesse, Dr. Libor Seda and Mr. Omar Naeem for their continual help and support both in Canada and during my work in Germany.

My friends in the McAuley group and others at Queen's University, for all the valuable discussions and advice when you should have been working on your own projects.

My brother Andrew, who is living his dream, and who taught me nearly everything I know about programming. Without your extensive tutelage, I would still be debugging my Predici code!

My dear parents, who did not always fully understand my occasional frustrations, but supported me regardless and never failed to say the things I needed to hear.

MITACS and MPRIME for their financial support.

Co-authorship

The material in Chapter 2 has been published in the refereed journal "Macromolecular Reaction Engineering". I prepared the drafts of the manuscript, performed all of the calculations, ran all of the related simulations and generated all of the Figures and Tables. Dr. Kim McAuley and I are co-authors on the paper. She provided technical advice throughout the course of the work, helping to investigate trends model predictions and scrutinize the model structure. She also helped edit the paper and thesis for clarity and completeness. Dr. McAuley was an active participant in discussions with me concerning modeling approaches and the analysis and interpretation of the model predictions. Chapter 3 represents a draft of second paper which will also be submitted to "Macromolecular Reaction Engineering", and Dr. McAuley will be a co-author on this paper as well.

Table of Contents

Chapter 1 -	- Intro	duction	
	1.1	Introduction.	
	1.2	References	
Chapter 2 -	- Mode	eling the Thern	nally Initiated Styrene Polymerization
-	2.1	Abstract	
	2.2	Introduction.	
		2.2.1	Thermal Polymerization
		2.2.2	Autoacceleration
		2.2.3	Literature Parameter Values
		224	Literature Data 1
		2.2.1	Parameter Selection and Estimation 1
	23	Model Imple	mentation 2
	2.5	2 3 1	Predici Implementation 2
		2.3.1	Estimability Analysis and Parameter Estimation 2
	2.4	2.J.Z Decults and F	Disquesion
	2.4		Decomptor Doubling and Estimation Deculta
		2.4.1	Parameter Kanking and Estimation Results
		2.4.2	Reparameterization and Hand-Tuning of
		• • •	Autoacceleration Parameters
		2.4.3	Parameter Re-estimation 3
		2.4.4	Assessing the Influence of High-Temperature
			Degradation Reactions
	2.5	Conclusions.	
	2.6	References	
Chapter 3 -	- Mode	eling the Chem	ically Initiated Styrene Polymerization
	3.1	Abstract	
	3.2	Introduction.	
	3.3	Model Devel	opment and Initial Parameter Values 5
	3.4	Simulation R	esults and Parameter Estimation
		3.4.1	Predictions of Thermal Polymerization Data
		3.4.2	Stationary-State Hypothesis on Initial Adduct
			Concentration. 6
		3.4.3	Parameter Ranking and Estimation Using All Thermal
			Polymerization Data
		3.4.4	Parameter Ranking and Estimation Using Thermally and
			Chemically Initiated Polymerization Data 6
		345	Model Adjustment via Hand Tuning of Important
		5.1.0	Parameters 7
		346	Hand Tuning of Mid-Chain Scission Kinetic
		5.1.0	Parameters 7
		3 1 7	Implementation of Transfer to Monomer Reaction 7
		2.4.9	Importance of Chain Saission and Transfer to Monomer
		3.4.0	Departiente of Cham-Scission and Transfer-to-Wohomer
	25	Conclusion	Nearli Ullis
	3.5	Conclusions a	and kecommendations
	3.6 C	References	
Chapter 4 -	- Conc	lusions and Re	commendations
	4.1	Conclusions.	
	4.2	Recommenda	ations for Future Work
	4.3	References	

Appendix 1 – Use of Predici	94
Appendix 2 – Peroxide-induced Mid-chain Scission Kinetics	107
Appendix 3 – Detailed Results from Parameter Estimation Studies using Combined Data	
from Thermal and Chemical Initiation Studies	111
from Thermal and Chemical Initiation Studies	111

List of Tables

Table 2.1	Reaction mechanism for the thermally initiated polymerization of styrene	10
Table 2.2	Equations describing the effect of diffusion control on kinetic coefficients.	12
Table 2.3	Addition adjustable parameters used in styrene polymerization model	13
Table 2.4	Constants and variables used in model equations	14
Table 2.5	Initial literature values for kinetic parameters	16
Table 2.6	Estimability analysis algorithm for parameter ranking	20
Table 2.7	Ranked parameter list and parameter estimates. These results were used to	
	generate the curve in Figure 2.1 and black curves in Figure 2.2.	28
Table 2.8	Final estimated parameter values	34
Table 3.1	Kinetic mechanism for chemically and thermally initiated polymerization	
	of styrene	47
Table 3.2	Initiator decomposition kinetic parameters (k _{dDCPo} , k _{dBPOo}) reported by	
	various authors	47
Table 3.3	Model equations describing the diffusion control of important kinetic rate	• •
	coefficients	53
Table 3 4	Literature values for kinetic parameters	58
Table 3.5	Initial values and bounds for reparameterized parameters	59
Table 3.6	Parameters used in diffusion-control equations.	61
Table 3 7	Calculated variables and physical constants	63
Table 3.8	Ranked parameter list with parameter estimates after implementation of	02
14010 5.0	SSH on initial concentration Initial values were taken from Chapter 2	67
Table 3.9	Ranked parameter list with parameter estimates fitted against full set of	07
	literature data	68
Table 3 10	Values of hand-tuned parameters that were adjusted to improve trends in	00
14010 5.10	conversion and molecular weight predictions	71
Table 3 11	Ranked list of parameters after reduction of mid-chain scission reactions	, 1
14010 5.11	and implementation of transfer-to-monomer reaction using estimated	
	narameter values from Section 3.4.4 as initial guesses and results of	
	parameter estimation Note that values shown in hold were estimated in	
	this attempt	74
Table A 2 1	Values of calculated and predicted terms used for calculation of κ .	109
Table A 3 1	Ranked list of parameters using estimated values from Chapter 2 as initial	107
100011.5.1	ouesses	117
Table A 3 2	Ranked list of parameters using estimated values from fitting of thermally	11,
100011.5.2	initiated experimental data and results of parameter estimation Attempt 1	125
Table A 3 3	Ranked list of parameters after hand tuning transfer-to-adduct initiator	120
14010 11.5.5	decomposition and autoacceleration onset parameters and results of	
	narameter estimation Attempt 2	137
Table 4 3 4	Ranked list of parameters after hand tuning autoacceleration strength	137
1 4010 / 1.2.4	narameters and results of parameter estimation Attempt 3	148
Table A 3 5	Ranked list of parameters after hand tuning of mid-chain seission	170
1 4010 1 1.5.5	narameters and results of parameter estimation Δ ttempt Δ	155
	parameters and results of parameter commation Attempt 7	155

Table A.3.6	Ranked list of parameters after implementation of transfer-to-monomer	
	reaction and results of parameter estimation Attempt 5	166
Table A.3.7	Ranked list of parameters after implementation of transfer-to-monomer	
	reaction using estimated parameter values from Attempt 4 as initial	
	guesses and results of parameter estimation Attempt 6	176

List of Figures

Figure 1.1	Skeleton structure of polystyrene (PS)	2
Figure 2.1	Full two-step thermal initiation mechanism. Diels-alder adduct indicated	8
Figure 2.2	Characteristic 1:3 backbiting, followed by β -scission to yield a dimer	
-	fragment and a living polymer chain	9
Figure 2.3	Sum-of-squared errors (J) versus the number of parameters estimated.	29
	Note that Wu's algorithm indicates that four parameters should be	
	estimated	
Figure 2.4	Fits comparing experimental data (\Diamond , $\circ^{[1]}$) to model predictions with initial	
	parameter guesses (—) and after four parameters are estimated (—). All	
	data are from bulk, thermally-initiated styrene polymerization	
	experiments. (a) 100 °C ^[1] ; (b) 100 °C ^[1] ; (c) 122.5 °C ^[2] ; (d)140 °C ^[1] ; (e)	
	$150 {}^{\circ}\mathrm{C}^{[3]}$; (f) 160 ${}^{\circ}\mathrm{C}$: (\Diamond) ^[3] , (\circ) ^[1] ; (g) 165 ${}^{\circ}\mathrm{C}^{[1]}$; (h) 170 ${}^{\circ}\mathrm{C}^{[3]}$. Note the	
	arrows indicating the autoacceleration onset points	31
Figure 2.5	Fits comparing experimental data (\Diamond , $\circ^{[1]}$) to model predictions after	
	manual tuning of diffusion control onset parameters and reestimation (—).	
	(a) $100 ^{\circ}C^{[1]}$; (b) $100 ^{\circ}C^{[1]}$; (c) $122.5 ^{\circ}C^{[2]}$; (d) $140 ^{\circ}C^{[1]}$; (e) $150 ^{\circ}C^{[3]}$; (f)	
	$160 ^{\circ}C^{[3],[1]}; (g) 165 ^{\circ}C^{[1]}; (h) 170 ^{\circ}C^{[3]}$	35
Figure 2.6	Comparison between model predictions with Campbell's degradation	
	reactions active (), and inactive () at 170 °C. Note that the dashed line	
	representing the predictions without the degradation reactions is nearly	
	hidden behind the solid black line	37
Figure 3.1	Thermal decomposition of a BPO initiator to two primary radicals	46
Figure 3.2	Peroxide-facilitated mid-chain hydrogen abstraction followed by β -	
	scission	48
Figure 3.3	Comparisons between experimental conversion (0), M_n (0), and M_w (1)	
	data and model predictions (conversion and M_n , —; M_w ,) using	
	parameter values estimated by Woloszyn and McAuley. ^[4] Data are from	
	bulk, thermally-initiated styrene polymerization experiments at 120 °C	
	that were not used in parameter estimation. ^[1] The initial adduct	
	concentration was assumed to be 0 mol L ⁻¹	64
Figure 3.4	Comparisons between experimental conversion (\Diamond), M_n (\Diamond), and M_w (\Box)	
	data and model predictions using updated estimated parameter values (,	
). Data are from bulk, thermally-initiated styrene polymerization	
	experiments at 120 °C. ¹¹	67
Figure 3.5	Comparisons between experimental conversion (\Diamond), M_n (\Diamond), and M_w (\Box)	
	data and model predictions () obtained using parameter values from	
	the first attempt at estimation using thermally and chemically initiated	
	polymerization data. (a, b) Selected thermal polymerization data at 160	
	$^{\circ}C^{\circ}$; (c, d) Selected DCP-initiated polymerization data at 130 $^{\circ}C$, (4000	
	ppm DCP) ¹³¹ ; (d, e) Selected BPO-initiated polymerization data at 90 $^{\circ}$ C,	

Figure 2.6	$(3050 \text{ ppm BPO})^{[5]}$	69
Figure 5.0	data and model predictions (—,) obtained using hand-tuned parameter values shown in Table 10. (a, b) Selected thermal polymerization data at 160 °C ^[3] ; (c, d) Selected DCP-initiated polymerization data at 130 °C, (4000 ppm DCP) ^[3] ; (d, e) Selected BPO-initiated polymerization data at 90 °C, (3050 ppm BPO) ^[5]	71
Figure 3.7	Comparisons between experimental conversion (\diamond), M_n (\diamond), and M_w (\Box) data and model predictions (—,) obtained using parameter values estimated using thermally and chemically initiated polymerization data after reduction of mid-chain scission reactions and implementation of transfer-to-monomer reaction. (a, b) Selected thermal polymerization data at 160 °C ^[3] ; (c, d) Selected DCP-initiated polymerization data at 130 °C, (4000 ppm DCP) ^[3] ; (d, e) Selected BPO-initiated polymerization data at 90 °C, (3050 ppm BPO) ^[5] .	76
Figure A.2.1 Figure A.3.1	In(κ _{strue}) vs. 1/T for PS chain scission via DTBP radical attack Comparisons between model predictions using the parameter values shown in the third column of Table A.3.1 (—) and conversion (◊, Δ), M _n (◊), M _w (□) and MWD (◊) data collected in thermal initiation styrene polymerization studies. (a) 100 °C ^[1] ; (b) 100 °C ^[1] ; (c) 100 °C ^[1] ; (d) 120 °C ^[1] ; (e) 120 °C ^[1] ; (f) 140 °C ^[1] ; (g) 140 °C ^[1] ; (h) 150 °C ^[3] ; (i) 150 °C ^[3] ; (j) 160 °C (Δ) ^[1] , (◊) ^[3] ; (k) 160 °C ^[3] ; (l) 165 °C ^[1] ; (m) 170°C ^[3] ; (n) 170°C ^[3] .	109
Figure A.3.2	Comparisons between model predictions after implementation of SSH on $[AH]_{\circ}$ (—) and conversion (\diamond , Δ), M_n (\diamond), M_w (\Box) and MWD (\diamond) data collected in thermal initiation styrene polymerization studies. (a) 100 °C ^[1] ; (b) 100 °C ^[1] ; (c) 100 °C ^[1] ; (d) 120 °C ^[1] ; (e) 120 °C ^[1] ; (f) 140 °C ^[1] ; (g) 140 °C ^[1] ; (h) 150 °C ^[3] ; (i) 150 °C ^[3] ; (j) 160 °C (Δ) ^[1] , (\diamond) ^[3] ; (k) 160 °C ^[3] ; (l) 165 °C ^[1] ; (m) 170°C ^[3] ; (n) 170°C ^[3] .	115
Figure A.3.3	Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.3.1 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation styrene polymerization studies. (a) 100 °C ^[1] ; (b) 100 °C ^[1] ; (c) 100 °C ^[1] ; (d) 120 °C ^[1] ; (e) 120 °C ^[1] ; (f) 140 °C ^[1] ; (g) 140 °C ^[1] ; (h) 150 °C ^[3] ; (i) 150 °C ^[3] ; (j) 160 °C (Δ) ^[1] , (\Diamond) ^[3] ; (k) 160 °C ^[3] ; (l) 165 °C ^[1] ; (m) 170°C ^[3] ; (n) 170°C ^[3] ;	119
Figure A.3.4	Comparisons between model predictions using the parameter values shown in the last column of Table A.3.1 (—) and conversion (\diamond , Δ), M _n (\diamond), M _w (\Box) and MWD (\diamond) data collected in chemical initiated styrene polymerization studies. (a) 120 °C, (DCP, 4000 ppm) ^[3] ; (b) 120 °C, (DCP, 4000 ppm) ^[3] , (c) 130 °C, (DCP, 4000 ppm) ^[3] ; (d) 130 °C, (DCP, 4000 ppm) ^[3] ; (e) 130 °C, (DCP, 4000 ppm) ^[3] ; (f) 140 °C, (DCP, 4000 ppm) ^[3] ; (g) 140 °C, (DCP, 4000 ppm) ^[3] ; (h) 140 °C, (DCP, 4000 ppm) ^[3] ; (i) 150 °C, (DCP, 4000 ppm) ^[3] ; (j) 150 °C, (DCP, 4000 ppm) ^[3] ; (k) 90 °C, (BPO,	
Figure A.3.5	Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.3.2 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI ^[1] ; (b) 100 °C, TI ^[1] ; (c) 100 °C, TI ^[1] ; (d) 120 °C, TI ^[1] ; (e) 120 °C, TI ^[1] ; (f) 140 °C, TI ^[1] ; (g) 140 °C, TI ^[1] ; (h) 150 °C, TI ^[3] ; (i) 150 °C, TI ^[3] ; (j) 160	122

°C, TI (Δ)^[1], (\Diamond)^[3]; (k) 160 °C, TI^[3]; (l) 165 °C, TI^[1]; (m) 170 °C, TI^[3]; (n) 170°C, TI^[3]; (o) 120 °C, CI [DCP, 4000 ppm]^[3]; (p) 120 °C, CI [DCP, 4000 ppm]^[3]; (q) 130 °C, CI [DCP, 4000 ppm]^[3]; (r) 130 °C, C] [DCP, 4000 ppm] 4000 ppm]^[3]; (s) 130 °C, CI [DCP, 4000 ppm]^[3]; (t) 140 °C, CI [DCP, 4000 ppm]^[3]; (u) 140 °C, CI [DCP, 4000 ppm]^[3]; (v) 140 °C, CI [DCP, 4000 ppm]^[3]; (w) 150 °C, CI [DCP, 4000 ppm]^[3]; (x) 150 °C, CI [DCP, 4000 ppm]^[3]; (x) 90 °C, CI [BPO, 3050 ppm]^[5]; (z) 90 °C, CI [BPO, 3050 ppm]^[5]..... 129 Comparisons between model predictions using the hand-tuned parameter Figure A.3.6 values shown in the third column of Table A.3.3 (—) and conversion (\diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[3]; (i) 150 °C, TI^[3]; (j) 160 °C, TI (Δ)^[1], (\diamond)^[3]; (k) 160 °C, TI^[3]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[3]; (n) 170°C, TI^[3]; (o) 120 °C, CI [DCP, 4000 ppm]^[3]; (p) 120 °C, CI [DCP, 4000 ppm]^[3]; (q) 130 °C, CI [DCP, 4000 ppm]^[3]; (r) 130 °C, CI [DCP, 4000 ppm]^[3]; (r) 140 °C, CI [DCP, 4000 ppm]^[3]; (t) 140 °C, CI [DCP, 4000 p 4000 ppm^[3]; (u) 140 °C, CI [DCP, 4000 ppm^[3]; (v) 140 °C, CI [DCP, 4000 ppm]^[3]; (w) 150 °C, CI [DCP, 4000 ppm]^[3]; (x) 150 °C, CI [DCP, 4000 ppm]^[3]; (x) 150 °C, CI [DCP, 4000 ppm]^[3]; (y) 90 °C, CI [BPO, 3050 ppm]^[5]; (z) 90 °C, CI [BPO, 3050 ppm]^[5]..... 135 Comparisons between model predictions using the estimated parameter Figure A.3.7 values shown in the last column of Table A.3.3 (—) and conversion (\Diamond, Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, $TI^{[1]}$; (c) 100 °C, $TI^{[1]}$; (d) 120 °C, $TI^{[1]}$; (e) 120 °C, $TI^{[1]}$; (f) 140 °C, $TI^{[1]}$; (g) 140 °C, $TI^{[1]}$; (h) 150 °C, $TI^{[3]}$; (i) 150 °C, $TI^{[3]}$; (j) 160 °C, TI $(\Delta)^{[1]}$, $(\delta)^{[3]}$; (k) 160 °C, TI^[3]; (l) 165 °C, TI^[1]; (m) 170 °C, TI^[3]; (n) $(11, 12)^{(11)}, (0)^{(11)},$ 4000 ppm]^[3]; (s) 130 °C, CI [DCP, 4000 ppm]^[3]; (t) 140 °C, CI [DCP, 4000 ppm]^[3]; (v) 140 °C, CI [DCP]; (v) 140 °C]; (v) 140 4000 ppm]^[3]; (w) 150 °C, CI [DCP, 4000 ppm]^[3]; (x) 150 °C, CI [DCP, 4000 ppm]^[3]; (x) 150 °C, CI [DCP, 4000 ppm]^[3]; (y) 90 °C, CI [BPO, 3050 ppm]^[5]; (z) 90 °C, CI [BPO, 3050 ppm]^[5]..... 141 Figure A.3.8 Comparisons between model predictions using the hand-tuned parameter values shown in the third column of Table A.3.4 (—) and conversion (\diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[3]; (i) 150 °C, TI^[3]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[3]; (k) 160 °C, TI^[3]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[3]; (n) 170°C, TI^[3]; (o) 120 °C, CI [DCP, 4000 ppm]^[3]; (p) 120 °C, CI [DCP, 4000 ppm]^[3]; (q) 130 °C, CI [DCP, 4000 ppm]^[3]; (r) 130 °C, CI [DCP, 4000 p 4000 ppm]^[3]; (s) 130 °C, CI [DCP, 4000 ppm]^[3]; (t) 140 °C, CI [DCP, 4000 ppm]^[3]; (u) 140 °C, CI [DCP, 4000 ppm]^[3]; (v) 140 °C, CI [DCP, 4000 ppm]^[3]; (w) 150 °C, CI [DCP, 4000 ppm]^[3]; (x) 150 °C, CI [DCP, 4000 ppm]^[3]; (y) 90 °C, CI [BPO, 3050 ppm]^[5]; (z) 90 °C, CI [BPO, 3050 ppm]^[5]..... 146

Х

Figure A.3.9	Comparisons between model predictions using the hand tuned parameter values shown in the third column of Table A.3.5 (—) and conversion (\diamond , Δ), M_n (\diamond), M_w (\Box) and MWD (\diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI ^[1] ; (b) 100 °C, TI ^[1] ; (c) 100 °C, TI ^[1] ; (d) 120 °C, TI ^[1] ; (e) 120 °C, TI ^[1] ; (f) 140 °C, TI ^[1] ; (g) 140 °C, TI ^[1] ; (h) 150 °C, TI ^[3] ; (i) 150 °C, TI ^[3] ; (j) 160 °C, TI (Δ) ^[1] , (\diamond) ^[3] ; (k) 160 °C, TI ^[3] ; (l) 165 °C, TI ^[1] ; (m) 170 °C, TI ^[3] ; (n) 170 °C, TI ^[3] ; (o) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (p) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (s) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (t) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (
	4000 ppm] ^[3] ; (w) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (y) 90 °C, CI [BPO, 3050 ppm] ^[5] ; (z) 90 °C,	153
Figure A.3.10	Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.3.5 (—) and conversion (\Diamond, Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI ^[1] ; (b) 100 °C, TI ^[1] ; (c) 100 °C, TI ^[1] ; (d) 120 °C, TI ^[1] ; (e) 120 °C, TI ^[1] ; (f) 140 °C, TI ^[1] ; (g) 140 °C, TI ^[1] ; (h) 150 °C, TI ^[3] ; (i) 150 °C, TI ^[3] ; (j) 160 °C, TI (Δ) ^[1] , (\Diamond) ^[3] ; (k) 160 °C, TI ^[3] ; (l) 165 °C, TI ^[1] ; (m) 170°C, TI ^[3] ; (n) 170°C, TI ^[3] ; (o) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (p) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (s) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (t) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (t) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (t) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (w) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (w) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (y) 90 °C, CI [DCP, 4000 ppm] ^[5] ; (z) 90 °C, CI [DCP, 4000 ppm] ^[5] .	159
Figure A.3.11	Comparisons between model predictions using the hand-tuned parameter values shown in the third column of Table A.3.6 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI ^[1] ; (b) 100 °C, TI ^[1] ; (c) 100 °C, TI ^[1] ; (d) 120 °C, TI ^[1] ; (e) 120 °C, TI ^[1] ; (f) 140 °C, TI ^[1] ; (g) 140 °C, TI ^[1] ; (h) 150 °C, TI ^[3] ; (i) 150 °C, TI ^[3] ; (j) 160 °C, TI (Δ) ^[1] , (\Diamond) ^[3] ; (k) 160 °C, TI ^[3] ; (l) 165 °C, TI ^[1] ; (m) 170°C, TI ^[3] ; (j) 160 °C, TI (Δ) ^[1] , (\Diamond) ^[3] ; (k) 160 °C, TI ^[3] ; (l) 165 °C, TI ^[1] ; (m) 170°C, TI ^[3] ; (n) 170°C, TI ^[3] ; (o) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (p) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (p) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (r) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (s) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (v) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (w) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (w) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (w) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (y) 90 °C, CI [BPO, 3050 ppm] ^[5] ; (z) 90 °C, CI [BPO, 3050 ppm] ^[5]	164
Figure A.3.12	Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.3.6 (—) and conversion (\Diamond , Δ), M _n (\Diamond), M _w (□) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI ^[1] ; (b) 100 °C, TI ^[1] ; (c) 100 °C, TI ^[1] ; (d) 120 °C, TI ^[1] ; (e) 120 °C, TI ^[1] ; (f) 140 °C, TI ^[1] ; (g) 140 °C, TI ^[1] ; (h) 150 °C, TI ^[3] ; (i) 150 °C, TI ^[3] ; (j) 160 °C, TI (Δ) ^[1] , (\Diamond) ^[3] ; (k) 160 °C, TI ^[3] ; (l) 165 °C, TI ^[1] ; (m) 170°C, TI ^[3] ; (n) 170°C, TI ^[3] ; (o) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (p) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (r) 130 °C, CI [DCP,	104

	4000 ppm] ^[3] ; (s) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (t) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (u) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (v) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (w) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 90 °C, CI [BPO, 3050 ppm] ^[5] ; (z) 90 °C, CI [BPO, 3050 ppm] ^[5] .	170
Figure A.3.13	Comparisons between model predictions using the hand tuned values shown in the third column of Table A.3.7 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI ^[1] ; (b) 100 °C, TI ^[1] ; (c) 100 °C, TI ^[1] ; (d) 120 °C, TI ^[1] ; (e) 120 °C, TI ^[1] ; (f) 140 °C, TI ^[1] ; (g) 140 °C, TI ^[1] ; (h) 150 °C, TI ^[3] ; (i) 150 °C, TI ^[3] ; (j) 160 °C, TI (Δ) ^[1] , (\Diamond) ^[3] ; (k) 160 °C, TI ^[3] ; (l) 165 °C, TI ^[1] ; (m) 170°C, TI ^[3] ; (n) 170°C, TI ^[3] ; (o) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (p) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (g) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (r) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (s) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (t) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (u) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (w) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (y) 90 °C, CI [BPO, 3050 ppm] ^[5] ; (z) 90	175
Figure A.3.14	Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.2.7 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI ^[1] ; (b) 100 °C, TI ^[1] ; (c) 100 °C, TI ^[1] ; (d) 120 °C, TI ^[1] ; (e) 120 °C, TI ^[1] ; (f) 140 °C, TI ^[1] ; (g) 140 °C, TI ^[1] ; (h) 150 °C, TI ^[3] ; (i) 150 °C, TI ^[3] ; (j) 160 °C, TI (Δ) ^[1] , (\Diamond) ^[3] ; (k) 160 °C, TI ^[3] ; (l) 165 °C, TI ^[1] ; (m) 170°C, TI ^[3] ; (o) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (p) 120 °C, CI [DCP, 4000 ppm] ^[3] ; (r) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (s) 130 °C, CI [DCP, 4000 ppm] ^[3] ; (t) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (u) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (v) 140 °C, CI [DCP, 4000 ppm] ^[3] ; (w) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (w) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (x) 150 °C, CI [DCP, 4000 ppm] ^[3] ; (y) 90 °C, CI [DCP, 4000 ppm] ^[5] ; (z) 90 °C, CI [DCP, 4000 ppm] ^[5] .	181

Nomenclature

Symbol	Description	Units
a	root-mean-squared end-to-end distance per square root of the number of monomer units	m num ^{-1/2}
А	adjustable parameter for the onset of the 2 nd stage of diffusion control	dimensionless
A _{cr}	adjustable parameter for the onset of the 2 nd stage of diffusion control	$(kg/mol)^{-1/2}$
A _{crm}	adjustable parameter for the onset of the 3 rd stage of diffusion control	dimensionless
В	adjustable parameter for the 3 rd stage of diffusion control	dimensionless
С	adjustable parameter for the 4 th stage of diffusion control	dimensionless
C ₁	adjustable parameter for the 4 th of diffusion control (DCP initiation)	dimensionless
C ₂	adjustable parameter for the 4 th of diffusion control (BPO initiation)	dimensionless
Cp	concentration of polymer in the system	$mol L^{-1}$
C _{rRatio}	adjustable parameter for the onset of diffusion control for thermal initiation	dimensionless
C _{rRatioDCP}	adjustable parameter for the onset of diffusion control for DCP initiation	dimensionless
C _{rRatioBPO}	adjustable parameter for the onset of diffusion control for BPO initiation	dimensionless
E _{cr}	adjustable parameter for the onset of 2 nd stage of diffusion control	cal/mol
E _{crm}	adjustable parameter for the onset of the 3 rd stage of diffusion control	cal/mol
\mathbf{f}_{i}	efficiency factor for thermally induced radical initiation	dimensionless
f _{DCP}	efficiency factor for DCP induced radical initiation	dimensionless
f _{BPO}	efficiency factor for BPO induced radical initiation	dimensionless
jc	number of monomer units between entanglement nodes on a polymer chain	num.
k _{n eff}	effective-diffusion-limited propagation rate coefficient	$L \text{ mol}^{-1} \text{ s}^{-1}$
k _T	effective-translational diffusion-limited termination rate coefficient	L mol ⁻¹ s ⁻¹
k _{tDCP,eff}	effective-diffusion-limited termination-by-DCP-radical rate coefficient	L mol ⁻¹ s ⁻¹
k _{tBPO,eff}	effective-diffusion-limited termination-by-BPO-radical rate coefficient	$L \text{ mol}^{-1} \text{ s}^{-1}$
k _{t,eff}	effective-overall diffusion-limited termination rate coefficient	$L \text{ mol}^{-1} \text{ s}^{-1}$
k _{t,seg}	effective-segmental diffusion-limited termination rate coefficient	$L \text{ mol}^{-1} \text{ s}^{-1}$
k _{t,rd}	effective-reactional diffusion-limited termination rate coefficient	$L \text{ mol}^{-1} \text{ s}^{-1}$
K	critical variable for the onset of the 1 st stage of diffusion control	$kg^{0.5} mol^{-0.5}$

V	x^{1}	
K _{cr}	control	$kg^{0.5}$ mol ^{-0.5}
n	coefficient for translational diffusion limited termination	dimensionless
m	coefficient for critical parameter	dimensionless
[M]	concentration of styrene in the system	mol L ⁻¹
MW	molecular mass of styrene	kg mol ⁻¹
M	weight average molecular weight of dead polymer chains	kg mol ⁻¹
IVI _W	weight-average molecular weight of dead polymer chains	kg moi
WIwcr	at the enset point of the 1 st stage of diffusion control	kg mol ⁻¹
D	at the onset point of the 1 stage of unfusion control	aal V ⁻¹ mal ⁻¹
K T		
	temperature	<u> </u>
I g,m	glass transition temperature of styrene	<u> </u>
$T_{g,p}$	glass transition temperature of polystyrene	K
$ m V_{f}$	total system free volume	dimensionless
V _{f,m}	fractional free volume of styrene in the system	dimensionless
$V_{f,p}$	fractional free volume of polystyrene in the system	dimensionless
V_{fer}	free volume at the onset point of the 1 st stage of diffusion	dimonsionloss
	control	unnensionness
V_{fcreff}	adjustable parameter for the onset of the 4 th stage of diffusion control	dimensionless
Vform	free volume at the onset point of the 2^{nd} stage of diffusion	
· ici,iii	control	dimensionless
V _{fcrmo}	adjustable parameter for the onset of the 3 rd stage of diffusion	dimensionless
V _{g,m}	specific free volume of styrene at its glass transition	dimensionless
N/		
V _{g,p}	temperature	dimensionless
V_m^*	specific free volume required for one jumping unit of	dimensionless
	styrene	
V_{p}^{*}	specific free volume required for one jumping unit of	dimensionless
P	polystyrene	
Х	fractional conversion of styrene	dimensionless
a	thermal expansion coefficient for styrene	volume/K
α _n	thermal expansion coefficient for polystyrene	volume/K
δ_{a}	segmental diffusion parameter for styrene	[/σ
<u>ی</u>	Lennard-Iones diameter for a styrene molecule	
 	weight fraction of styrene in the system	dimensionless
0 m	weight fraction of polystyrene in the system	dimensionless
ωn		annensioniess

References

- [1] A.W. Hui, A.E. Hamielec, *Journal of Applied Polymer Science*, **1972**, *16*, 749.
- [2] G.V. Korolev, M.P. Berezin, V.P. Grachev, I.N. Zyuzin, *Polymer Science Series A*, **2006**, *49*, 3, 421.
- [3] C. Kotoulas, A. Krallis, P. Pladis, C. Kiparissides, *Macromolecular Chemistry and Physics*, **2003**, *204*, 1305.
- [4] J.D. Woloszyn, K.B. McAuley, *Macromolecular Reaction Engineering*, **2011**, *5*, 9-10, 453.
- [5] M.A. Villalobos, A.E. Hamielec, P.E. Wood, *Journal of Applied Polymer Science*, **1993**, 50, 327.

Chapter 1 – Introduction

1.1 Introduction

Over the last half-century, mathematical modeling has become an indispensible tool for the development and control of polymerization processes. With improvements in computing power, it has become possible to develop and solve complex models describing polymerization reactions. Improved software tools that can help to facilitate the model development process are now available. For example, Predici[™] by CiT[™] contains a large library of chemical reactions commonly encountered in polymerization systems, which it uses to facilitate the development of complex polymerization models.^[1] Instead of focusing modeling efforts on the repeated derivation of balance equations for each chemical species, modelers can use their time to investigate the importance of candidate reactions and to determine appropriate values for parameters.^[2]

Detailed polymerization models can easily contain 30 or more parameters related to rates of chemical reaction. It is often difficult to determine which parameter values should be tuned to obtain a better fit to experimental data and which should remain at values obtained from previous studies reported in the literature, where available. Selection of parameters for estimation is still often carried out manually, based on the modeler's intuition concerning the relative importance of each parameter and the reliability of its literature value.^[3-7] The large number of parameters and correlation between the effects of parameters can make this task exceedingly difficult. In recent years, statistical methods have been developed to assist modelers in determining which parameters they should estimate.^[8-11] These techniques have recently been used to aid parameter estimation in polymerization models.^[8, 9, 12]

The main objective of this research project is to develop an industrially relevant model describing the synthesis of polystyrene (PS, shown in Figure 1.1). The model should be capable of accurately predicting conversion, number- and weight-average molecular weight and molecular weight distribution. This comprehensive model needs to include important phenomena observed during styrene polymerization at conditions used in large-scale expandable polystyrene production. As such, two commonly-used peroxide initiators, dicumyl peroxide (DCP) and biphenyl peroxide (BPO), are considered. Thermal initiation of styrene is included in the model because the adduct species involved in thermal PS initiation can also influence molecular weight behaviour.^[13, 14] The effect of viscosity on kinetic parameters commonly referred to as the Trommsdorff effect or autoacceleration is also included in the model. Since industrial styrene polymerizations may be run to very high conversions in the presence of reactive peroxide species, peroxide-induced mid-chain scission reactions are also included in the model.



Figure 1.1 – Skeleton structure of polystyrene (PS).

Chapter 2 describes the first step towards developing this comprehensive model. A polymerization model is developed in Predici[™], based on the current literature concerning initiator-free (thermal) polymerization of styrene. Thermal polymerization of styrene is used for these preliminary investigations to keep model complexity at a modest level and to limit the number of possible reaction mechanisms and adjustable kinetic parameters. This initial thermal polymerization model, containing 40 adjustable parameters, provides a useful case study problem for gaining experience with recently-developed statistical tools for parameter ranking, selection and estimation before larger-scale models and data sets are considered.^[15, 16]

In Chapter 3, the model is extended to include reactions involving DCP and BPO initiators. Because average molecular weights and molecular weight distributions can be extremely important in determining the final physical properties of the PS material, particular effort is made to fit the model to molecular weight data from the literature. Assumptions concerning initial adduct concentration, mid-chain scission reactions and chain-transfer to monomer are investigated. These investigations are facilitated by the automatic model generation provided by Predici[™] and by the aforementioned parameter selection and estimation techniques.

In the final stage of this work, the parameter selection and estimation tools are applied using a large industrial data set to obtain improved parameter values and test model predictions. The Predici[™] model is extended to include additional chemical initiator species used in the industrial production of PS and to include the effects of blowing

agents such as *n*-pentane. This final stage is not included in the current thesis to protect the intellectual property of the sponsoring company.

Chapter 4 of the thesis provides the main conclusions resulting from the research described in Chapters 2 and 3 along with recommendations for future work.

1.2 References

- [1] M. Wulkow, *Predici: Simulation Package for Polyreactions*. 2003: Rastede, Germany.
- [2] M. Wulkow, *Macromolecular Reaction Engineering*, **2008**, *2*, 6, 461.
- [3] E. Saldivar-Guerra, J. Bonilla, G. Zacahua, M. Abores-Velasco, *Journal of Polymer Science: Part A: Polymer Chemistry*, **2006**, *44*, 6962.
- [4] Y. Fu, M.F. Cunningham, R.A. Hutchinson, *Macromolecular Reaction Engineering*, **2007**, 1, 243.
- [5] L. Bentein, D.R. D'hooge, M. Reyniers, G.B. Marin, *Macromolecular Theory and Simulation*, **2011**, *20*, 238.
- [6] J. Belincanta-Ximenes, P.V.R. Mesa, L.M.F. Lona, E. Vivaldo-Lima, N.T. McManus, A. Penlidis, *Macromolecular Theory and Simulation*, **2007**, *16*, 194.
- [7] B. Boutevin, D. Bertin, *European Polymer Journal*, **1999**, *35*, 815.
- [8] K.Z. Yao, B.M. Shaw, B. Kou, K.B. McAuley, D.W. Bacon, *Polymer Reaction Engineering*, 2003, 11, 3, 563.
- [9] D.E. Thompson, K.B. McAuley, P.J. McLellan, *Macromolecular Reaction Engineering*, **2009**, *3*, 130.
- [10] S. Wu, K.B. McAuley, T.J. Harris, *Canadian Journal of Chemical Engineering*, **2009**,
- [11] S. Wu, T.J. Harris, K.B. McAuley, *The Canadian Journal of Chemical Engineering*, **2011**, *89*, 148.
- [12] H. Karimi, M.A. Schaffer, K.B. McAuley, *Macromolecular Reaction Engineering*, **2011**, *submitted*.
- [13] O.F. Olaj, H.F. Kauffmann, J.W. Breitenbach, *Makromoleculare Chemie*, **1976**, *177*, 3065.
- [14] O.F. Olaj, H.F. Kauffmann, J.W. Breitenbach, H. Bieringer, *Polymer Letters Edition*, **1977**, 15, 229
- [15] M.A. Villalobos, A.E. Hamielec, P.E. Wood, *Journal of Applied Polymer Science*, **1993**, *50*, 327.
- [16] C. Kotoulas, A. Krallis, P. Pladis, C. Kiparissides, *Macromolecular Chemistry and Physics*, 2003, 204, 1305.

Chapter 2 – Modeling the Thermally Initiated Polymerization of Styrene

2.1 Abstract

A model is developed to describe the bulk thermally-initiated free-radical polymerization of styrene between 100 °C and 170 °C. The detailed model structure accounts for generation and consumption of the styrene adduct. Chain transfer to adduct, rather than chain transfer to monomer, is the only transfer reaction used in the model. Autoacceleration is modeled using the break-point method of Hui and Hamielec.^[1] Key model parameters are selected for estimation using a ranking algorithm that prioritizes adjustable parameters according to the size of their influences on model predictions, as well as uncertainties in initial parameter values. The algorithm also accounts for correlation between effects of parameters, a problem often encountered in polymerization models. Using this parameter ranking and selection technique,^[2, 3] 4 of the 40 model parameters are selected for estimation to improve the fit between model predictions and the data. After estimating the values of these parameters and adjusting two additional autoacceleration parameters by hand to ensure good prediction of the onset point for autoacceleration, the model predicts conversion data with a standard error of 5 %, and provides excellent fit to a MWD curve for a single experiment at 100 °C. Simulation results confirm that high-temperature backbiting and β -scission reactions^[4, 5] are not important in the temperature range of interest.

2.2 Introduction

Determining appropriate values for the parameters in a polymerization model can be one of the most difficult and time-consuming phases of model development. Values for parameters that appear in the model equations are not always well known or available from the literature. Also, sometimes different literature sources give significantly different values for the same kinetic parameters.^[6, 7] This chapter describes a modeling case study focused on determining whether model equations and parameter values from the literature are able to accurately describe the bulk thermal polymerization of styrene. Since many researchers have published model equations and data for this system, it is a good candidate for study.^[1, 4, 5, 7-10] A second objective for this work is to demonstrate how recently-developed techniques can be used to determine which model parameters should remain at their literature values and which should be adjusted to improve the model fit to the data.

2.2.1 Thermal Polymerization

Thermal polymerization, wherein free radicals are generated by decomposition of monomer, is another important phenomenon that arises during the bulk polymerization of styrene, particularly at temperatures above 150 °C.^[1, 11] Table 2.1 provides a set of chemical reactions from the literature which is used to develop the model used in the current case study. Thermal initiation is assumed to occur via a three-step process in Reaction 1 through 3. It is common to assume that the radicals A* and M* generated by Reaction 2 have the same reactivity towards monomer in Reaction 3 and 4.^[12-14] This

mechanism has been adopted because it is recognized as the most plausible means of generating free radicals from styrene, and is shown in Figure 2.1.^[11, 15]



Figure 2.1 – Full two-step thermal initiation mechanism. Diels-alder adduct indicated.

Note that many modelers have used a simpler third-order initiation scheme that was first proposed by Hui and Hamielec wherein Reaction 1 and 2 are combined so that three monomers react directly to produce two radical molecules.^[1, 8, 16] The Hui and Hamielec mechanism is attractive because a single rate coefficient is required in place of k_1 , k_{-1} and k_i . One benefit of using the more detailed scheme in Table 2.1 is that the concentration of adduct, AH, is predicted by the model. Chain transfer to adduct (Reaction 8) is an important reaction that can influence MWD.^[17] Note that Hui and Hamielec and other modelers employed a chain-transfer-to-monomer reaction in their models to match experimental molecular weights.^[1, 13, 18] The mechanism in Table 2.1 does not include chain transfer to styrene as it has been shown that chain transfer to adduct is by far the dominant chain-transfer reaction.^[17, 19] Note that depropagation (reverse of Reaction 5) and other chain-end degradation reactions (Reaction 9 through 12) are included in Table 2.1 because Campbell and Morbidelli determined that these reactions can be important at

high temperatures (e.g., > 200 °C)^[4, 5]. These reactions are included to assess whether they will have a noticeable effect on molecular weight distributions at the upper end of the temperature range of interest (i.e., 170 °C). A sample backbiting and β -scission reaction is shown in Figure 2.2.



Figure 2.2 – Characteristic 1:3 backbiting, followed by β -scission to yield a dimer fragment and a living polymer chain.

An efficiency factor, f_i, is applied in Reaction 2 to account for side reactions that consume primary radicals A^{*} and M^{*} before they are able to propagate with monomer. Some literature models account for the fact that short radicals tend to propagate more rapidly than longer radicals.^[20] This effect is neglected in the current model for simplicity and because all of the data sets are primarily concerned with formation of high-molecular weight polymer.

Reaction Type	Reaction	Number
Adduct Formation	$M + M \xrightarrow[k_{-1}]{k_1} AH$	1
Adduct Radical Formation	$AH + M \xrightarrow{k_i} A^* + M^*$	2
Adduct Initiation	$A^* + M \xrightarrow{fast} P_1$	3
Adduct Initiation	$M^* + M \xrightarrow{fast} P_1$	4
Propagation	$P_n + M \xrightarrow[k_{-p}]{k_p} P_{n+1}$	5
Termination by Combination	$P_n + P_m \xrightarrow{k_{tc}} D_{n+m}$	6
Termination by Disproportionation	$P_n + P_m \xrightarrow{k_{td}} D_n + D_m$	7
Chain Transfer to Adduct	$P_n + AH \xrightarrow{k_{fd}} D_n + A^*$	8
1:3 Backbiting/β- scission	$P_n \xrightarrow{k_{1b}} P_{n-2} + D_2$	9
1:5 Backbiting/β-	$P_n \xrightarrow{k_{2b}} P_{n-3} + D_3$	10
scission	$P_n \xrightarrow{k_{2b}} D_{n-2} + P_2$	11
1:7 Backbiting/β- scission	$P_n \xrightarrow{k_{3b}} P_{n-4} + D_4$	12

Table 2.1. Reaction mechanism for the thermally initiated polymerization of styrene

2.2.2 Autoacceleration

Autoacceleration, which is an important phenomenon in bulk styrene polymerization, occurs due to a sharp increase in system viscosity at high conversion.^[21] The increased viscosity limits the diffusion of molecules through the reaction mixture, especially the diffusion of large polymeric radicals, resulting in reduced rates for termination reactions. As such, modelers need to account for the effect of diffusion on reaction rates so that their models can provide accurate predictions of polymerization rates and molecular weight distributions (MWDs). A recent review by Achilias describes efforts by various modelers

to describe autoacceleration mathematically.^[22] Vivaldo-Lima et al. showed that the break-point method of Hui and Hamielec^[1] outlined in Table 2.2 can successfully describe the entire course of a free-radical styrene polymerization, providing a better fit to data than the continuous autoacceleration model proposed by Chiu et al.,^[23] which requires additional parameters to account for direct effects of viscosity on diffusion coefficients.^[24] Literature values for parameters and physical constants used in the expressions in Table 2.2 are provided in Table 2.3 and Table 2.4.

Equation Re	ef. No.
Additional Equation used in First Stage of Diffusion Control	<u>ol</u>
$k_{t,seg} = k_{to} (1 + \delta_c C_p M W) $ ^[1]	0] (2.1)
Additional Equations used in Second Stage of Diffusion	
Control	
$K = M_{w}^{m} e^{\left(\frac{A}{V_{f}}\right)} $ ^{[2}	5] (2.2)
$K_{cr} = A_{cr} e^{\left(\frac{E_{cr}}{RT}\right)} $ ^{[2}	5] (2.3)
$V_{f} = \sum_{i=1}^{3} \omega_{i} V_{i}^{*} V_{f,i} $ ^[26,]	.27] (2.4)
$V_{f,i} = V_{g,i} + \alpha_i (T - T_{g,i})$ [26,	(2.5)
$k_{\rm T} = k_{\rm to} \left(\frac{M_{\rm w,cr}}{M_{\rm w}}\right)^n e^{\left[-A\left(\frac{1}{V_{\rm f}} - \frac{1}{V_{\rm f,cr}}\right)\right]}$ ^[1]	^{0]} (2.6)
$k_{t,rd} = k_{t,rd,min}X + k_{t,rd,max}(1 - X)$ ^[2]	8] (2.7)
$k_{t,rd,min} = A_{min}k_{p,eff}[M]$ ^[2]	7] (2.8)
$k_{t,rd,max} = A_{max}k_{p,eff}[M]$	7] (2.9)
$A_{\min} = \frac{4}{3}\pi a^2 \sigma$	^{9]} (2.10)
$A_{\rm max} = \frac{8}{3}\pi a^3 j_c^{1/2} $ ^[2]	^{9]} (2.11)
$k_{t,eff} = \left(\frac{1}{k_{t,seg}} + \frac{1}{k_T}\right)^{-1} + k_{t,rd}$ ^[3]	^{0]} (2.12)
Additional Equations used in Third Phase of Diffusion Cont	<u>rol</u>
$V_{\rm f,crm} = A_{\rm crm} e^{\left(\frac{-E_{\rm crm}}{RT}\right)} $ ^[10]	(2.13)
$k_{p,eff} = k_{po} \exp\left[-B\left(\frac{1}{V_{f}} - \frac{1}{V_{f,crM}}\right)\right]$ ^[2]	5] (2.14)
Additional Equation used in Fourth Phase of Diffusion Cont	<u>rol</u>
$fi = f_{0i} \exp\left[-C\left(\frac{1}{V_f} - \frac{1}{V_{f,creff}}\right)\right]$ ^[10,]	(2.15)

Table 2.2. Equations describing the effect of diffusion control on kinetic coefficients.

Symbol	Name	Initial Value	Units	Uncertainty	Ref.
a	root-mean-squared end-to-end distance per square root of the number of monomer units	7.5x10 ⁻¹⁰	m num ^{-1/2}	50%	[31]
А	adjustable parameter for the onset of the 2 nd stage of diffusion control	3.48x10 ⁻¹	dimensionless	50%	[16]
A _{cr}	adjustable parameter for the onset of the 2^{nd} stage of diffusion control	2.99x10 ⁻¹	(kg/mol) ^{-1/2}	50%	[16]
A _{crm}	adjustable parameter for the onset of the 3 rd stage of diffusion control	3.11x10 ⁻¹	dimensionless	50%	[16]
В	adjustable parameter for the 3 rd stage of diffusion control	1	dimensionless	50%	[16]
С	adjustable parameter for the 4 th stage of diffusion control	1	dimensionless	50%	[16]
E _{cr}	adjustable parameter for the onset of 2^{nd} stage of diffusion control	3.83×10^3	cal/mol	50%	[16]
E _{crm}	adjustable parameter for the onset of the 3 rd stage of diffusion control	1.67×10^3	cal/mol	50%	[16]
jc	number of monomer units between entanglement nodes on a polymer chain	175	num.	10%	[32, 33]
n	coefficient for translational diffusion limited termination	1.75	dimensionless	10%	[16]
m	coefficient for critical parameter	0.5	dimensionless	10%	[16]
V _{fcreff}	adjustable parameter for the onset of the 4 th stage of diffusion control	6.9x10 ⁻²	dimensionless	50%	[16]
V _m *	specific free volume required for one jumping unit of styrene	9.12x10 ⁻¹	dimensionless	50%	[7]
V_p^*	specific free volume required for one jumping unit of polystyrene	8.25x10 ⁻¹	dimensionless	50%	[7]
α _m	thermal expansion coefficient for styrene	1x10 ⁻³	volume/K	10%	[16]
α _p	thermal expansion coefficient for polystyrene	4.8x10 ⁻⁴	volume/K	10%	[16]
δ _c	segmental diffusion parameter for styrene	1x10 ⁻³	L/g	10%	[16]
σ	Lennard-Jones diameter for a styrene molecule	7.4x10 ⁻¹⁰	m	10%	[16]

Table 2.3. Additional adjustable parameters used in styrene polymerization model.

Symbol	Name	Value	Units	Ref.
MW	molecular mass of styrene	0.10415	kg mol ⁻¹	
T _{g,m}	glass transition temperature of styrene	185	K	[16]
T _{g,p}	glass transition temperature of polystyrene	378	K	[16]
V _{g,m}	specific free volume of styrene at its glass transition temperature	2.5x10 ⁻²	dimensionless	[16]
$V_{g,p}$	specific free volume of polystyrene at its glass transition temperature	2.5x10 ⁻²	dimensionless	[16]
R	universal gas constant 1.9859		cal K ⁻¹ mol ⁻¹	
Т	temperature		K	
M _w	weight-average molecular weight of dead polymer chains		kg mol ⁻¹	
K	critical variable for the onset of the 1 st stage of diffusion control		kg ^{0.5} mol ^{-0.5}	
K _{cr}	critical constant for the onset of the 1 st stage of diffusion control		kg ^{0.5} mol ^{-0.5}	
V _f	total system free volume		dimensionless	
V _{f,m}	fractional free volume of styrene in the system		dimensionless	
V _{f,p}	fractional free volume of polystyrene in the system		dimensionless	
V _{fcr}	free volume at the onset point of the 1 st stage of diffusion control		dimensionless	
M _{wcr}	weight-average molecular weight of dead polymer chains at the onset point of the 1 st stage of diffusion control		kg mol ⁻¹	
ω _m	weight fraction of styrene in the system		dimensionless	
ω _p	weight fraction of polystyrene in the system		dimensionless	
X	fractional conversion of styrene		dimensionless	
[M]	concentration of styrene in the system		mol L ⁻¹	
Cp	concentration of polymer in the system		mol L ⁻¹	
k _{t,seg}	effective-segmental diffusion-limited termination rate coefficient		L mol ⁻¹ s ⁻¹	
k _T	effective-translational diffusion-limited termination rate coefficient		L mol ⁻¹ s ⁻¹	
k _{t,rd}	effective-reactional diffusion-limited termination rate coefficient		L mol ⁻¹ s ⁻¹	
k _{t,eff}	effective-overall diffusion-limited termination rate coefficient		L mol ⁻¹ s ⁻¹	
k _{p,eff}	effective-diffusion-limited propagation rate coefficient		L mol ⁻¹ s ⁻¹	
V _{fcr,m}	free volume at the onset point of the 2 nd stage of diffusion control		dimensionless	
\mathbf{f}_{i}	efficiency factor for thermally induced radical initiation		dimensionless	

Table 2.4. Constants and variables used in model equations.

Equation (2.1) through (2.15) in Table 2.2 describe how the kinetic parameters, k_p , k_{tc} , k_{td} and f_i are affected by changes in the total available free volume in the system.^[1, 10, 25-27, 29] In the initial stage of the polymerization, when available free volume is large, all molecules diffuse freely through the reaction mixture. However, as polymer chains increase in size, they coil around themselves, increasing the polymer concentration gradient across the coils, leading to the outward segmental diffusion of the polymer chain ends, which leads to a mild increase in the rate of chain termination, which is accounted for by Equation (2.1).^[16, 28, 34] During this first stage of diffusion-controlled polymerization, all other rate coefficients remain at the chemically-controlled values in Table 2.5.

As polymerization proceeds further, the population of long polymeric chains begins to increase, which increases the system viscosity. At a critical point (i.e., when $K = K_{cr}$ as computed using Equation (2.2) and (2.3)), termination reactions become diffusion controlled. The expression involving k_T , $k_{t,seg}$ and $k_{t,rd}$ in Equation (2.12) is used to account for the three contributions to the overall termination rate coefficient by each of the modes of diffusion.^[30] This second stage of diffusion control leads to the onset of autoacceleration during which the rate of termination decreases but the rate of propagation for individual chains remains high. Onset of the third stage of diffusion control is defined as the point at which the total free volume in the system decreases to a critical free volume, $V_{f,crm}$. At this stage, movement of small molecules becomes hindered by high viscosity which reduces the rate coefficient for propagation as shown in Equation (2.14). In the final stage of diffusion-controlled polymerization, viscosity reaches levels

high enough to severely inhibit the diffusion of initiator radicals, thereby reducing the efficiency factor f_i as shown in Equation (2.15).

2.2.3 Literature Parameter Values

Table 2.5 contains literature values for rate coefficients and activation energies for the reactions in Table 2.1. Approximate uncertainties for the parameters are also shown. It is assumed that parameters that were fitted using conversion and molecular weight data have uncertainty levels of 40% of their nominal values^[4, 31-33, 35, 36] and that parameters obtained using pulsed-laser polymerization or other direct experimental techniques are more accurate.^[6, 37]

Parameter	Value at Reference Temperature	E _a /R (K)	Uncertainties	T _{ref} (°C)	Ref.
k ₁	2.27x10 ⁻⁹	$1.12 \text{x} 10^4$	15%, 10%	101.25	[38]
k_1/k_{-1}	4.23×10^{-3}	6.50×10^3	100%	120	[13]
ki	5.09x10 ⁻⁶	1.20×10^3	100%	120	[13]
k _p	2.06×10^3	3.91×10^3	5%	120	[37]
k _{-p}	1.62	$1.06 \text{x} 10^4$	10%	120	[4]
k _{tc}	1.56×10^{8}	7.53×10^2	30%	120	[6]
k _{td}	$2.24 \text{x} 10^7$	7.53×10^2	30%	120	[6]
k _{fd}	7.03×10^2	9.39×10^3	500%	120	[15, 39, 40]
k _{1b}	5.02×10^{-1}	9.25×10^3	10%	120	[4]
k _{2b}	1.39	9.25×10^3	10%	120	[4]
k _{3b}	1.030×10^{-2}	9.25×10^3	10%	120	[4]
fi	0.7		25%		[35, 36]

Table 2.5. Initial literature values for kinetic parameters.

Table 2.1 does not contain mechanistic steps related to controlled radical polymerization of styrene because the current model is focused on conventional thermal polymerization. Note, however, that recent kinetic studies involving nitroxide-mediated styrene polymerization provide useful information about rate coefficients for thermal initiation reactions.^[12, 14, 38, 41-44] For example, Kothe and Fischer devised a method to determine the

rate coefficient for formation of styrene adduct (forward Reaction 1 in Table 2.1) by monitoring the nitroxide concentration in the initial stages of a nitroxide-mediated polymerization.^[38] Kothe and Fischer's rate coefficient and activation energy agree well with values determined by Moad et al.^[45] and Kirchner et al.^[46, 47] In Table 2.5, Kothe and Fischer's estimates for k_{1o} and $(E_a/R)_1$ are selected as initial parameter values and assigned relatively small uncertainties of 15% and 10%, respectively, based on linear regression results presented by the authors. Saldivar-Guerra et al. used values from thirdorder kinetic parameters^[1] to determine that k_1 should lie between about $1x10^{-6}$ and $5x10^{-6}$ s⁻¹ at 125 °C.^[12] In the current model, rather than estimating k_1 , the approach of Kotoulas et al.^[13] is followed and the ratio k_1/k_1 is estimated. Combining Kothe's values for k_1 and $(E_a/R)_1$ with Kotoulas's value of k_1/k_1 results in $k_1 = 7.5x10^{-6}$ s⁻¹ at 125 °C. This value is similar to the range of values calculated by Saldivar-Guerra et al.

Greszta and Matyjaszewski found that simulations neglecting chain-transfer reactions yielded molecular weight predictions ~100 times higher than those measured experimentally.^[44] Inclusion of a chain-transfer-to-monomer mechanism in their reaction scheme (using a rate constant of 0.28 L mol⁻¹ s⁻¹)^[48] did not significantly lower the predicted molecular weights. Upon addition of a chain-transfer-to-adduct reaction, desired molecular weights were predicted using their estimated value of 50 L mol⁻¹ s⁻¹ at 120 °C. The authors note that this large value is justified experimentally in light of the work by Olaj et al.^[19] Note that Pryor and Coco estimated an even higher value of the chain-transfer-to-adduct rate coefficient (i.e., $k_{fd} = 150$ L mol⁻¹ s⁻¹ at 60 °C)^[39], which can be extrapolated to ~700 L mol⁻¹ s⁻¹at 120 °C using their estimated activation energy of 28 kJ mol⁻¹.^[40] This activation energy falls into the range of reasonable values (~25 - 38 kJ mol⁻¹) obtained from quantum chemical calculations.^[15] Considering the significant disparity between the various estimated rate coefficient values for k_{fd} , an uncertainty of 5 times the nominal value reported by Pryor and Coco is assigned.

In addition to the rate coefficients and activation energies in Table 2.5, the model described in this article contains 18 additional parameters associated with the equations that account for diffusion-controlled reaction rates (shown in Table 2.2) and the resulting autoacceleration behaviour. Initial literature values for these parameters and the associated uncertainties are provided in Table 2.3.

2.2.4 Literature Data

Hui and Hamielec^[1], Korolev et al.^[9] and Kotoulas et al.^[13] obtained bulk thermal polymerization data at temperatures between 100 °C and 170 °C. These data include 8 conversion vs. time profiles (including replicate results from experiments at 160 °C) and one MWD (obtained at 100 °C) that can be used for parameter fitting.

2.2.5 Parameter Selection and Estimation

Deciding which parameters to fit in this polymerization model and in similar models can be a difficult task for many reasons. Some parameters have more influence on model predictions than others. The effects of some parameters are often highly correlated with the effects of other parameters, making it difficult or impossible to estimate some of the parameters uniquely.^[49, 50] Also, polymerization models tend to have complicated response surfaces with respect to their parameters. As a result, many local minima are possible in the least-squares objective function used for parameter estimation, making it difficult to find the global optimum within the allowable parameter space.^[51]

Many modelers prefer to select a few parameters to adjust (by hand or using an optimization algorithm) so that model predictions can better match the data.^[52-54] Some modelers are hesitant to adjust parameter values that have been reported in the literature, unless conflicting values have been reported in several studies. Recent work by Saldivar-Guerra et al. illustrates the traditional approach to parameter selection and estimation.^[12] Their model describes thermal polymerization of styrene at 125 °C, mediated by 2.2,4,4tetramethyl-1-piperidinyloxy (TEMPO) and incorporates the two-step thermal initiation scheme shown in Table 2.1. They estimated two parameters, k_{-1} and k_h (the rate coefficient for chain transfer to TEMPO). Saldivar-Guerra et al. used their judgment to select these parameters based on uncertainty in their initial values and influence on model predictions. They chose to keep k_1 fixed at 1.33×10^{-8} L mol⁻¹ s⁻¹ because estimating this parameter resulted in only minor changes to the predictions and because they were confident in experimental methods used by Kothe and Fischer to obtain this value.^[38] The remaining kinetic parameters in their model were held at literature values. Fortunately, the two parameters selected for estimation had nearly independent influence on the model predictions, so that they could be easily estimated together.

Recent developments in parameter estimation techniques have yielded formal statistical methods for determining which parameters can and should be estimated from experimental data and which parameters should remain at their initial values (e.g., values reported in the literature for similar systems). Yao et al. developed the deflation

algorithm, shown in Table 2.6, which ranks model parameters according to their influence on model predictions.^[2, 55] After using this technique, influential parameters appear at the top of the ranked list and parameters that have little influence on predictions of the data appear near the bottom. This estimability ranking algorithm also accounts for correlation between the effects of different parameters, so that when two parameters influence model predictions in nearly the same way, only one of these parameters appears near the top of the list. After ranking the parameters, the modeler must then decide how many parameters to estimate. Estimating too many parameters can lead to numerical difficulties during parameter estimation, and estimating too few can lead to a poor fit to the experimental data.^[2] Additionally, Thompson et al. improved Yao's estimability ranking algorithm by introducing scaling factors that account for uncertainties in initial parameter values and uncertainties in measurements used for parameter fitting.^[55]

Table 2.6. Estimability analysis algorithm for parameter ranking.^[2, 55]

- **1.** Generate the sensitivity matrix Z.
- 2. Calculate the magnitude (sum of squared elements) for each column in the scaled sensitivity matrix, Z. The most estimable parameter corresponds to the column in Z with the largest magnitude. Set counter k to 1.
- 3. Put the k columns from Z for parameters that have been ranked into matrix X_k . Use X_k to predict columns in Z using least squares: $\hat{Z}_k = X_k (X_k^T X_k)^{-1} X_k^T Z$. Calculate the residual matrix: $R_1 = Z - \hat{Z}_1$. [Calculate the

magnitude of each column in R_k . The $(k+1)^{th}$ -most estimable parameter corresponds to the column in R_k with the largest magnitude.]

- 4. Increase k by 1, and put the columns corresponding to the k+1 parameters that have been ranked in matrix X_k .
- 5. Advance the iteration counter (subscripts for X and R) and repeat Steps 3 and 4 until all parameters are ranked or until it is impossible to calculate \hat{Z} in Step 3 due to matrix singularity.

The first step of the ranking algorithm is to generate the sensitivity matrix, Z. This matrix will have p columns, corresponding to the number of model parameters and N rows, corresponding to the number of data values available for model fitting. Each element of the scaled Z matrix is of the form:

$$\frac{\partial y_i}{\partial \theta_j} \cdot \frac{s_{\theta j}}{s_{yi}},$$
 (2.16)

where $\partial y_i / \partial \theta_j$ reflects a change in the prediction of the ith measured value as a result of a change in the jth parameter. These partial derivatives can be determined by solving sensitivity equations^[56] or using difference approximations (i.e., by perturbing parameter values and observing changes in model predictions).^[57] In Equation (2.16), $s_{\theta j}$ is a scaling factor related to the uncertainty in the initial value of parameter θ_j , and s_{yi} is a scaling factor related to the uncertainty in measurement y_i . Note that these uncertainty factors could be standard deviations computed from prior studies, or they may be user-selected values that reflect the modeler's beliefs about ranges of reasonable values for different parameters and reproducibility of measurements. Since the units of $s_{\theta j}$ and s_{yi} are the same as those of the associated parameters and measurements, the scaled sensitivity coefficients in Equation (2.16) are dimensionless.

The second step in the algorithm determines the top-ranked parameter, which has the largest scaled influence on the model predictions. Note that each column in Z contains derivatives with respect to a particular parameter. As a result, columns with many large positive or negative values correspond to parameters that have a large influence on model
predictions. In the third step, the column from Z corresponding to the top-ranked parameter becomes matrix X_1 , which is used to determine \hat{Z}_1 , the best least-squares fit to the columns of Z. A residual sensitivity matrix R_1 is computed to remove correlation with the top-ranked parameter. The column from R_1 with the largest magnitude corresponds to the second-most-estimable parameter. The ranking algorithm continues with the two columns from Z that correspond to the two most-estimable parameters in matrix X_2 .

Use of Thompson's uncertainty-based scaling factors enables the modeler to incorporate prior knowledge about the quality of initial parameter guesses. Influential parameters with larger uncertainties in their initial values appear near the top and are selected for estimation. Parameters that are already well known from previous studies tend to appear near the bottom of the ranked list and are not selected for estimation unless the available data set is very rich in information. These estimability analysis methods have been used to aid parameter estimation in models describing chemical and biological processes.^[55, 58-64]

Unfortunately, it has been difficult for modelers to decide on the appropriate number of parameters to estimate from the ranked list. Estimating too many parameters can lead to a large variance in model predictions and estimating too few parameters can lead to large bias because important parameters are fixed at incorrect values. Recently, Wu et al. developed a statistical method that can be used to determine the optimal number of parameters to estimate from the ranked list.^[65] Wu's method minimizes the expected mean-squared error in the model predictions by considering the tradeoff between variance and bias. Wu's method was recently used to select parameters for estimation in a liquid-

phase chemical reactor model with 9 parameters but has not been used for complex models with many parameters.^[66, 67] In the current research, this algorithm will be used to determine which of the 40 parameters that appear in Table 2.3 and Table 2.5 should be estimated.

The remainder of this article describes implementation of the model for thermallyinitiated bulk polymerization of styrene as well as parameter selection and estimation. The dynamic model equations are derived and solved using the polymer reaction modeling package Predici[™], which has been used to accelerate the modeling process.^[68] Model predictions are compared with the literature data, and recommendations are made regarding the importance of degradation reactions in the temperature range of interest.

2.3 Model Implementation

2.3.1 Predici Implementation

Predici[™] was used to implement the reaction mechanism shown in Table 2.1, along with the algebraic equations in Table 2.2. The main benefit of using Predici[™] is that the modeler can concentrate his or her efforts on development of the kinetic scheme, selection of mechanistic assumptions and parameter estimation instead of deriving (and rederiving) differential equations. Predici[™] generates all of the dynamic species balance equations required to simulate the polymerization using a library of available mechanisms. Additional algebraic equations, like those in Table 2.2, are implemented using function files that are coded by the modeler. For implementation of initiation (Reaction 2, 3 and 4 in Table 2.1), PrediciTM uses an overall free-radical initiation step that combines radical generation and the first propagation step, providing the option of including an efficiency factor, f. The quasi-stationary state assumption is used for primary radicals, yielding a generation rate for P₁ of $2fk_i$ [AH][M].

Occasionally, a particular reaction mechanism of interest is not available in the Predici[™] library and a work-around is required. For example, degradation reactions of the form:

$$P_n \xrightarrow{k_{2b}} D_{n-2} + P_2 \tag{2.17}$$

(Reaction 11 in Table 2.1) do not appear in Predici'sTM mechanism library. As shown below, this reaction can be simulated using two fictitious reactions in series:

$$P_n \xrightarrow{k_{2b}} P_{n-2} + F_2 \tag{2.18}$$

$$P_{n-2} + F_2 \xrightarrow{\text{fast}} D_{n-2} + P_2 \tag{2.19}$$

A large rate constant of 10 L mol⁻¹ s⁻¹ (~100 times larger than k_{2b}) is used for the second fictitious reaction to ensure that all of the fictitious dimer species, F_2 , generated during the simulation is immediately consumed. Note that the rate coefficient used for the first fictitious step is k_{2b} , the value of the rate coefficient for the real overall reaction.^[4, 5]

In the current model, Arrhenius expressions for kinetic rate coefficients are implemented in reparameterized form to facilitate parameter estimation:

$$\mathbf{k} = \mathbf{k}_{0} \mathbf{e}^{\left(\frac{-\mathbf{E}_{a}}{\mathbf{R}}\left(\frac{1}{\mathbf{T}} - \frac{1}{\mathbf{T}_{0}}\right)\right)},\tag{2.20}$$

rather than the traditional form:

$$\mathbf{k} = \mathbf{A}\mathbf{e}^{\left(\frac{-\mathbf{E}_a}{\mathbf{R}\mathbf{T}}\right)}.$$

 k_o in Equation (2.20) is the value of the rate coefficient when the reaction occurs at the reference temperature T_o . One benefit of using k_o as a model parameter (rather than the pre-exponential factor A) is that correlation between parameters is reduced.^[69-72]

2.3.2 Estimability Analysis and Parameter Estimation

After the model equations were implemented, and initial simulations performed using the literature values in Table 2.3 and Table 2.5, the next step was to determine which parameters should be adjusted to improve the model fit, using the estimability ranking algorithm in Table 2.6. The parametric sensitivity coefficients in the Z matrix were determined using difference approximations by running Predici[™] simulations with each parameter individually adjusted upward by 5 % from its initial value. The Object Embedding and Linking (OLE) functionality in Predici[™] was used to generate Excel[™] spreadsheets containing model predictions using the perturbed parameter values. Elements of the sensitivity matrix were calculated using Excel[™]. The sensitivity matrix was then imported into MATLAB[™] where the estimability ranking algorithm was

performed. After the parameters were ranked, the built-in parameter estimation capability of PrediciTM was used to fit the adjustable parameters, starting with the top-ranked parameter, then the top two parameters and so on. PrediciTM adjusted the parameters to minimize the objective function below:

$$J = \sum_{i=1}^{r} \sum_{j=1}^{d_i} \sum_{k=1}^{n_{ij}} \frac{\left(y_{m,ijk} - y_{ijk}\right)^2}{s_{yj}},$$
(2.22)

which is the scaled sum-of-squared errors between the model predictions, y_{ijk} , and measured data, $y_{m,ijk}$, from the r = 8 experimental runs available for parameter estimation. Note that $d_i = 2$ for the run at 100 °C because two different types of measurements (i.e., monomer concentration and MWD data) were used to fit the parameters and $d_i = 1$ for the runs at other temperatures where only conversion data were obtained. The number of data values of the particular type collected during each run is denoted by n_{ij} . The values of s_{yj} used in Equation (2.22) are the same measurement uncertainty values used to scale the sensitivity coefficients in Equation (2.16). Note that the weighted least-squares objective function in Equation (2.22) is slightly different than the default objective function used by PrediciTM. Information about how this objective function was implemented is provided in Appendix 1. The value of J was determined with different numbers of parameters estimated from the ranked list, and Wu's method was used to determine the optimal number of parameters to estimate.^[67]

2.4 Results and Discussion

2.4.1 Parameter Ranking and Estimation Results

Of the 40 parameters that appear in Table 2.3 and Table 2.5, 34 could be ranked using the algorithm in Table 2.6 before MatlabTM reported a matrix singularity when attempting to invert $X_{35}^T X_{35}$. This result indicates that severe numerical difficulties would be encountered if an attempt were made to estimate more than 34 parameters from the available data.^[1, 9, 13] The resulting ranked list of parameters is shown in Table 2.7. The six unranked parameters appear at the bottom of Table 2.7 in no particular order. k_{fdo} , which is the rate coefficient for transfer-to-adduct at 120 °C, was selected as the most estimable parameter.

_		Scaling			Estimated	
Parameter	Initial Value	Factor	Lower Bound	Upper Bound	Value	Rank
k _{fdo}	7.04×10^2	500%	5.0x10 ⁻¹	3.5×10^3	1.59×10^{3}	1
$(E_a/R)_{fd}$	3.37×10^3	500%	$2.0 \mathrm{x} 10^3$	$1.7 \mathrm{x} 10^4$	$4.54 \text{x} 10^3$	2
$(E_a/R)_i$	1.21×10^4	100%	$1.0 \mathrm{x} 10^3$	$1.0 \mathrm{x} 10^5$	$1.20 \mathrm{x} 10^4$	3
$(E_a/R)_{1/-1}$	$6.50 ext{x} 10^3$	100%	$6.0 \mathrm{x} 10^2$	$1.3 \text{x} 10^4$	$6.49 ext{x} 10^3$	4
k _{po}	2.06×10^3	5%	1.4×10^{3}	2.7×10^3		5
А	3.48x10 ⁻¹	50%	1.7x10 ⁻¹	5.2x10 ⁻¹		6
E _{crm}	1.67×10^3	50%	$8.4 \text{x} 10^2$	2.5×10^3		7
$(E_a/R)_{3b}$	9.25x10 ³	50%	$4.6 \text{x} 10^3$	$1.4 \mathrm{x} 10^4$		8
$(E_a/R)_1$	1.12×10^4	10%	$1.0 \mathrm{x} 10^4$	$1.2 \mathrm{x} 10^4$		9
k _{io}	5.08x10 ⁻⁶	100%	5.0x10 ⁻⁷	1.0x10 ⁻⁵		10
$(E_a/R)_{2b}$	9.25x10 ³	50%	$4.6 \text{x} 10^3$	$1.4 \mathrm{x} 10^4$		11
CrRatio	1.0	100%	0.0	1.0		12
(A) _{1/-1}	$6.40 ext{x} 10^4$	100%	6.0×10^3	1.3×10^5		13
$V_{\rm fpj}$	8.35x10 ⁻¹	50%	4.2x10 ⁻¹	1.3		14
V _{fmj}	9.12x10 ⁻¹	50%	4.6×10^{-1}	1.4		15
E _{cr}	3.83×10^3	50%	1.9×10^{3}	5.7×10^3		16
V _{fcrma}	3.11x10 ⁻¹	10%	2.8x10 ⁻¹	3.4x10 ⁻¹		17
k _{tdo}	2.24×10^7	30%	1.61×10^7	$2.9 \mathrm{x} 10^7$		18
k _{tco}	1.56×10^{8}	30%	1.1×10^{8}	$2.0 \mathrm{x} 10^8$		19
k _{1bo}	5.02×10^{-1}	50%	2.5x10 ⁻¹	7.x10 ⁻¹		20
δ _c	1.00×10^{-3}	10%	9.0x10 ⁻⁴	1.1x10 ⁻³		21
$(E_a/R)_{td}$	7.53×10^2	30%	$5.3 \text{x} 10^2$	9.8×10^2		22
\mathbf{f}_{i}	7.00x10 ⁻¹	25%	5.3x10 ⁻¹	8.8x10 ⁻¹		23
α _m	1.00x10 ⁻³	50%	5.0x10 ⁻⁴	1.5x10 ⁻³		24
$(E_a/R)_{1b}$	9.25×10^3	50%	$4.6 \text{x} 10^3$	$1.4 \mathrm{x} 10^4$		25
α _p	4.80x10 ⁻⁴	10%	4.3×10^{-4}	5.3x10 ⁻⁴		26
k ₁₀	2.2x10 ⁻⁹	15%	1.9x10 ⁻⁹	2.6x10 ⁻⁹		27
$(E_a/R)_{tc}$	7.53×10^2	30%	$5.3 x 10^2$	9.8×10^2		28
k _{2bo}	1.39	50%	7.0x10 ⁻¹	2.1		29
k _{pro}	1.62	10%	1.5	1.8		30
k _{3bo}	1.03x10 ⁻²	50%	5.1x10 ⁻³	1.5x10 ⁻²		31
$(E_a/R)_{pr}$	1.06×10^4	10%	9.5×10^3	$1.2 x 10^4$		32
В	1.00	50%	5.0x10 ⁻¹	1.5		33
С	1.00	50%	5.0x10 ⁻¹	1.5		34
$(E_a/R)_p$	3.91x10 ³					unranked
A _{cr}	8.11x10 ²					unranked
a	7.5x10 ⁻¹⁰					unranked
n	1.75					unranked
j.	1.75×10^2					unranked
σ	7.4x10 ⁻¹⁰					unranked

Table 2.7. Ranked parameter list and parameter estimates. These results were used to generate the curve in Figure 2.1 and black curve in Figure 2.2

The influence of the number of parameters estimated on the value of the objective function is shown in Figure 2.1. As expected, estimating additional parameters decreases the value of the objective function until it levels off after four or five parameters. Using Wu's technique, it was found that the top four parameters, k_{fdo} , $(E_a/R)_{fd}$, $(E_a/R)_i$ and $(E_a/R)_{1/-1}$ should be estimated to achieve the best model predictions and that the remaining 36 parameters should remain at their literature values.



Figure 2.3. Sum-of-squared errors (J) versus the number of parameters estimated. Note that Wu's algorithm indicates that four parameters should be estimated.

Estimation of these four parameters reduces the value of the weighed least-squares objective function by 76.6%, from 45300 to 10600, indicating a substantial improvement in the model fit to the data. Note that the four parameters selected for estimation are all associated with chain transfer to adduct and thermal initiation. The four parameters that were selected have a large influence on the model predictions and relatively large uncertainties in their initial values. The remaining 36 parameters were not selected because they either had little influence on predictions of the data (e.g., the entanglement spacing parameter j_c), their effects were highly correlated with the effects of higher

ranked parameters (e.g., the rate coefficient for thermal initiation at 120 °C, k_{io} is correlated with the $(E_a/R)_i$), or their initial uncertainties were small (e.g., the propagation rate coefficient at 120 °C, k_{po}). The resulting estimates for the four parameters are provided in the sixth column of Table 2.7.

Figure 2.2 shows comparisons of experimental measurements and model predictions. The gray solid lines in Figure 2.2 show model predictions using the initial parameter values and the black solid lines are the model predictions using parameter estimates from Table 2.7. In Figure 2.2(f), open diamonds and circles are used to indicate replicate experiments. Estimation of the four parameters resulted in improved fit to the single available MWD curve, which was obtained at 100 °C. The improved MWD fit was enabled by estimating the 1st- and 2nd-ranked parameters (k_{fdo} and (E_a/R)_{fd}), which are related to chain transfer to adduct. Noticeable improvements in fit were also achieved for the conversion data at higher temperatures (150 to 170 °C).



Figure 2.4. Fits comparing experimental data (\diamond , $\circ^{[1]}$) to model predictions with initial parameter guesses (—) and after four parameters are estimated (—). All data are from bulk, thermally-initiated styrene polymerization experiments. (a) 100 °C^[1]; (b) 100 °C^[1]; (c) 122.5 °C^[9]; (d)140 °C^[1]; (e) 150 °C^[13]; (f) 160 °C: (\diamond)^[13], (\circ)^[1]; (g) 165 °C^[1]; (h) 170 °C^[13]. Note the arrows indicating the autoacceleration onset points.

2.4.2 Reparameterization and Hand-tuning of Autoacceleration Parameters

Despite the improvement in model predictions after parameter estimation, there are still some concerns with model predictions and fit to the data in Figure 2.2. The main concern is the late onset of autoacceleration at higher temperatures (shown by arrows in Figure 2.2(f) and (h)). None of the three parameters (A, A_{cr} , and E_{cr}) that most influence the onset behaviour of autoacceleration was selected for estimation, presumably because the least-squares objective function in Equation (2.22) focuses only on vertical squared deviations between model predictions and data. Other subtle features, such as the change in slope at the autoacceleration onset point were afforded no special significance when fitting parameters, but they are important to model users when judging the validity of model predictions. A more complex objective function could have been implemented (e.g., with terms that penalize deviations between the measured and predicted slopes of the conversion vs. time curves). However, because of the relatively large uncertainties in the measured slopes due to sparse and noisy data (e.g., Figure 2.2(c)), no slope terms were used in the objective function for the current study.

Two of the parameters responsible for the onset of autoacceleration, A_{cr} and E_{cr} , govern the critical value, K_{cr} , which is computed using an Arrhenius expression (Equation (2.3) in Table 2.2). To facilitate adjustment of parameters in this expression, the equation was reparameterized to:

$$K_{cr} = K_{ref} e^{\left(\frac{E_{cr}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)}.$$
(2.23)

 K_{ref} and E_{cr} were then tuned manually until the onset of autoacceleration occurred at the correct location along the conversion profile for each of the seven experimental conditions. K_{ref} was adjusted to match the onset of autoacceleration at the reference temperature of 160 °C corresponding to the data in Figure 2.2(f), and then E_{cr} was adjusted to ensure a good match at higher and lower temperatures. During the hand-tuning process, the remaining 38 parameters were held at the values used to obtain the black lines in Figure 2.2. It should be noted that it was necessary to move E_{cr} to a value higher than the upper bound shown in Table 2.7. This requirement indicates that the parameter bounds used for estimation in PrediciTM may have been too narrow.

One additional concern is that the onset of diffusion control for initiation occurs before the onset of diffusion control for propagation (using either the literature values for the parameters or the updated values from Table 2.7). This type of behaviour is not consistent with diffusion-controlled kinetic theory.^[16, 21, 73] To address this problem, a new parameter, C_{eff} was defined as the ratio $V_{f,creff}/V_{f,crm}$. The initial guess and upper bound for this parameter were both set to 1 to ensure that the onset of diffusion control for initiation occurs concurrently with, or after, the onset of diffusion-controlled propagation. C_{eff} was then included as a model parameter in place of $V_{f,creff}$.

A second round of parameter ranking and estimation was performed to refine the parameter estimates, using the hand-tuned values of K_{ref} and E_{cr} as well as the constraint on C_{eff} .

2.4.3 Parameter Re-estimation

Parameters were reranked and reestimated, with the two manually tuned parameters, K_{ref} and E_{cr} , fixed at their hand tuned values of 7.0 kg^{1/2} mol^{-1/2} and 7.0x10³ cal mol⁻¹, respectively. The same four parameters $(k_{fdo}, (E_a/R)_{fd}, (E_a/R)_i)$ and $(E_a/R)_{1/-1}$ remained at the top of the ranked list. Use of Wu's method indicated that no additional parameters should be estimated. Upon re-estimation of these four parameters, there was a further 3.7% improvement in the objective function (from 10600 to 10200). Note that J = 10200is lower than the smallest value 10400 obtained for the objective function in Figure 2.1 with a large number of parameters estimated, indicating that the best fit in Figure 2.1 corresponded to a local minimum. Hand-tuning of the autoacceleration parameters helped the optimizer to find a better minimum, which may be the global minimum. Values for the re-estimated and hand-tuned parameters are shown in Table 2.8. Figure 2.3 compares the final model predictions using the values in Table 2.8 to experimental data. Good agreement is obtained between model predictions and measured data for both the conversion profiles and MWD curve, except for some mismatch in the conversion profile at 122.5 °C.

Parameter	Value
k _{fdo}	1.59×10^{3}
$(E_a/R)_{fd}$	$4.54 \text{x} 10^3$
$(E_a/R)_i$	$1.20 \mathrm{x} 10^4$
$(E_a/R)_{1/-1}$	5.92×10^3
K _{ref}	7.0
E _{cr}	7.0×10^3

Table 2.8. Final estimated parameter values.



Figure 2.5. Fits comparing experimental data (\diamond , $\circ^{[1]}$) to model predictions after manual tuning of diffusion control onset parameters and reestimation (—). (a) 100 °C^[1]; (b) 100 °C^[1]; (c) 122.5 °C^[9]; (d)140 °C^[1]; (e) 150 °C^[13]; (f) 160 °C^{[13],[1]}; (g) 165 °C^[1]; (h) 170 °C^[13].

2.4.4 Assessing the Influence of High-Temperature Degradation Reactions

At the start of this modeling work, it was not certain whether the high-temperature degradation reactions considered by Campbell et al. (i.e., reverse Reaction 5 and Reaction 9 through 12 in Table 2.1) would influence model predictions noticeably at temperatures up to 170 °C.^[4, 5] None of the parameters associated with these reactions was selected for estimation, indicating that adjusting the values of these parameters had little influence on predictions of the data. Figure 2.4 compares model predictions with and without these reactions for the highest-temperature experiment (at 170 °C). The solid curve, which corresponds to the results in Figure 2.3(h), nearly covers the dashed line corresponding to predictions with these reactions turned off. MWD predictions at 170 °C also showed negligible change. As a result, the model predictions confirm that the influence of hightemperature degradation reactions on conversion and molecular weight predictions is negligible in the temperature range of interest. Note that predictions (not shown) for the remaining data at lower temperatures were similarly unaffected by omission of the degradation reactions. As such, the degradation reactions will be omitted from future modeling work, which will focus on chemically-initiated styrene polymerization at temperatures up to 170 °C.



Figure 2.6. Comparison between model predictions with Campbell's degradation reactions active (—), and inactive (--) at 170 °C. Note that the dashed line representing the predictions without the degradation reactions is nearly hidden behind the solid black line.

2.5 Conclusions

A model was implemented in Predici[™] to describe the bulk thermally-initiated freeradical polymerization of styrene between 100 and 170 °C. The mechanism accounts explicitly for adduct generation and consumption. Chain transfer to adduct, rather than chain transfer to monomer, is the only chain-transfer reaction in the model. Equations governing changes in kinetic coefficients due to diffusion limitations are included to account for autoacceleration. Kinetic parameters from the literature result in reasonable predictions of available conversion vs. time and MWD behaviour. Selection of four parameters for reestimation improves the model fit significantly. This case study illustrates the usefulness of recently developed estimability analysis and parameter selection techniques. The four parameters selected are the rate coefficient for chaintransfer to adduct, and activation energies for transfer to adduct, primary-radical generation, and adduct decomposition to monomer. These parameters were selected using the estimability ranking algorithm based on their influence on model predictions, uncertainties in their literature values, and correlations among the effects of the parameters. Estimating more than four parameters resulted in a negligible improvement in the objective function for parameter estimation. Estimating additional parameters also caused an increase in the mean-squared error criterion for parameter selection, indicating that estimating additional parameters would not improve the model predictions. Hand tuning of two autoacceleration parameters enabled the parameter estimator to find a better local minimum, which may or may not be the global minimum. The model fits using the final parameter values reduced the objective function by 77.5 % compared to predictions made using the original literature values. Good fits were obtained for the single MWD curve (at 100 °C) and for conversion vs. time data collected between 100 and 170 °C. Predictions from the model were used to confirm that high-temperature thermal degradation reactions had little influence on the model predictions at 170 °C and below.

2.6 References

- [1] A.W. Hui, A.E. Hamielec, *Journal of Applied Polymer Science*, **1972**, *16*, 749.
- [2] K.Z. Yao, B.M. Shaw, B. Kou, K.B. McAuley, D.W. Bacon, *Polymer Reaction Engineering*, **2003**, *11*, 3, 563.
- [3] S. Wu, K.B. McAuley, T.J. Harris, *Canadian Journal of Chemical Engineering*, **2009**,
- [4] J.D. Campbell, F. Teymour, M. Morbidelli, *Macromolecules*, **2003**, *36*, 15, 5491.
- [5] J.D. Campbell, F. Teymour, M. Morbidelli, *Macromolecules*, **2003**, *36*, 15, 5502.
- [6] M. Buback, F.-D. Kuchta, *Macromolecular Chemistry and Physics*, **1997**, *198*, 1455.
- [7] A. Keramopoulos, C. Kiparissides, *Macromolecules*, **2002**, *35*, 4155.
- [8] D. Moscatelli, C. Cavalotti, M. Morbidelli, *Macromolecules*, **2006**, *39*, 9641.
- [9] G.V. Korolev, M.P. Berezin, V.P. Grachev, I.N. Zyuzin, *Polymer Science Series* A, **2006**, 49, 3, 421.
- [10] M.J. Scorah, R. Dhib, A. Penlidis, *Chemical Engineering Science*, **2006**, *61*, 4827.
- [11] F.R. Mayo, Journal of the American Chemical Society, **1968**, 90, 5, 1289.
- [12] E. Saldivar-Guerra, J. Bonilla, G. Zacahua, M. Abores-Velasco, *Journal of Polymer Science: Part A: Polymer Chemistry*, **2006**, *44*, 6962.
- [13] C. Kotoulas, A. Krallis, P. Pladis, C. Kiparissides, *Macromolecular Chemistry and Physics*, **2003**, *204*, 1305.
- [14] Y. Fu, M.F. Cunningham, R.A. Hutchinson, *Macromolecular Reaction Engineering*, 2007, 1, 243.
- [15] K.S. Khuong, W.H. Jones, W.A. Pryor, K.N. Houk, *Journal of the American Chemical Society*, 2005, 127, 1265.

- [16] J. Gao, A. Penlidis, *Reviews in Macromolecular Chemistry and Physics*, **1996**, *C36*, 2, 199.
- [17] O.F. Olaj, H.F. Kauffmann, J.W. Breitenbach, *Makromoleculare Chemie*, **1976**, *177*, 3065.
- [18] W.J. Yoon, J.H. Ryu, C. Cheong, K.Y. Choi, *Macromolecular Simulation and Theory*, **1998**, 7, 327.
- [19] O.F. Olaj, H.F. Kauffmann, J.W. Breitenbach, *Polymer Letters Edition*, **1977**, *15*, 229.
- [20] M.A. Villalobos, A.E. Hamielec, P.E. Wood, *Journal of Applied Polymer Science*, **1993**, *50*, 327.
- [21] S.K. Soh, D.C. Sundberg, *Journal of Polymer Science: Polymer Chemistry Edition*, **1982**, 20, 1299.
- [22] D.S. Achilias, Macromolecular Theory and Simulations, 2007, 16, 319.
- [23] W.Y. Chiu, W. Charratt, D.S. Soong, *Macromolecules*, **1983**, *16*, 348.
- [24] E. Vivaldo-Lima, A. Hamielec, P.E. Wood, *Polymer Reaction Engineering*, **1994**, 2, 1-2, 17.
- [25] F.L. Marten, A.E. Hamielec, *Journal of Applied Polymer Science*, **1982**, 27, 489.
- [26] C.M. Vrentas, J.L. Duda, *Journal of Polymer Science Part B Polymer Physics*, **1984**, 22, 3, 459.
- [27] D.S. Achilias, C. Kiparissides, *Macromolecules*, **1992**, *25*, 3739.
- [28] M.A. Dubé, J.B.P. Soares, A. Penlidis, A.E. Hamielec, *Industrial and Engineering Chemistry Research*, **1997**, *36*, 966.
- [29] G.T. Russel, D.H. Napper, R.G. Gilbert, *Macromolecules*, **1988**, *21*, 2133.
- [30] R.A. Hutchinson, A. Penlidis, *Free-Radical Polymerization: Homogeneous* Systems, in *Polymer Reaction Engineering*, Blackwell Publishing, Oxford, 2007, ch. 3, p. 118.

- [31] J.D. Ferry, Viscoelastic Properties of Polymers, 1970.
- [32] D. Schrader, *Physical Constants of Poly(styrene)*, in *Polymer Handbook*, 4th edition, John Wiley & Sons, 2005, ch. 5, p. 91.
- [33] L.J. Fetters, D.J. Lohse, R.H. Colby, *Chain Dimension and Entanglement Spacing*, in *Physical Properties of Polymers Handbook*, 2nd edition, Springer, Cincinnati, 2006, ch. 25, p. 447.
- [34] D. Bhattacharya, A.E. Hamielec, *Polymer*, **1986**, *27*, 611.
- [35] L. Cavin, A. Rouge, T. Meyer, A. Renken, *Polymer*, **2000**, *41*, 3925.
- [36] W.J. Yoon, K.Y. Choi, *Polymer*, **1992**, *33*, 21, 4582.
- [37] M. Buback, F.-D. Kuchta, Macromolecular Chemistry and Physics, 1995, 196, 1887.
- [38] T. Kothe, H. Fischer, *Journal of Polymer Science: Part A: Polymer Chemistry*, **2001**, *39*, 4009.
- [39] J.H. Coco, W.A. Pryor, *Macromolecules*, **1970**, *3*, 5, 500.
- [40] W.A. Pryor, L.D. Lasswell, Advances in Free-Radical Chemistry, 1975, 5, 27.
- [41] L. Bentein, D.R. D'hooge, M. Reyniers, G.B. Marin, *Macromolecular Theory and Simulation*, **2011**, *20*, 238.
- [42] J. Belincanta-Ximenes, P.V.R. Mesa, L.M.F. Lona, E. Vivaldo-Lima, N.T. McManus, A. Penlidis, *Macromolecular Theory and Simulation*, 2007, 16, 194.
- [43] B. Boutevin, D. Bertin, *European Polymer Journal*, **1999**, *35*, 815.
- [44] D. Greszta, K. Matyjaszewski, *Macromolecules*, **1996**, *29*, 7661.
- [45] G. Moad, E. Rizzardo, D.H. Solomon, *Polymer Bulletin*, **1982**, *6*, 589.
- [46] K. Kirchner, K. Buchholz, *Die Angewandte Makromolekulare Chemie*, **1970**, *13*, 178, 127.

- [47] K. Buchholz, K. Kirchner, *Die Makromolekulare Chemie*, **1976**, *177*, 935-938,
- [48] N.G. Saha, U.S. Nandi, S.R. Palit, Journal of the Chemical Society, 1958, 12.
- [49] K.Z. Yao, K.B. McAuley, E.K. Marchildon, *Journal of Applied Polymer Science*, 2003, 89, 3701.
- [50] B. Kou, K.B. McAuley, J.C.C. Hsu, D.W. Bacon, *Macromolecular Materials and Engineering*, **2005**, *290*, 537.
- [51] L.A. Polic, L.M. Lona, T.A. Duever, A. Penlidis, *Macromolecular Simulation and Theory*, **2004**, *13*, 115.
- [52] S. Santanakrishnan, L. Tang, R.A. Hutchinson, M. Stach, I. Lacík, J. Schrooten, P. Hesse, M. Buback, *Macromolecular Reaction Engineering*, **2010**, *4*, 499.
- [53] M. Buback, P. Hesse, R.A. Hutchinson, P. Kasák, I. Lacík, M. Stach, I. Utz, *Industrial and Engineering Chemistry Research*, **2008**, 47, 8197.
- [54] L. Hu, L. Wu, F. Song, B.-G. Li, *Macromolecular Reaction Engineering*, **2010**, *4*, 621.
- [55] D.E. Thompson, K.B. McAuley, P.J. McLellan, *Macromolecular Reaction Engineering*, **2009**, *3*, 130.
- [56] J.R. Leis, M.A. Kramer, Association for Computing Machinery Transactions on Mathematical Software, **1988**, 14, 1, 45.
- [57] A. Saltelli, K. Chan, E.M. Scott, *Sensitivity Analysis*, John Wiley & Sons Ltd., New York, 2000.
- [58] J.V. Littlejohns, K.B. McAuley, A.J. Daugulis, *Journal of Chemical Technology and Biotechnology*, **2009**, *85*, 2, 173.
- [59] B. Kou, K.B. McAuley, J.C.C. Hsu, D.W. Bacon, *Macromolecular Materials and Engineering*, **2005**, *290*, 537.
- [60] B.R. Jayasankar, A. Ben-Zvi, B. Huang, *Computers & Chemical Engineering*, **2009**, *33*, 484.

- [61] V.I. Koeva, S. Daneshvar, R.J. Senden, A.H.M. Imam, L.J. Schreiner, K.B. McAuley, *Macromolecular Theory and Simulation*, **2009**, *18*, 495.
- [62] H. Yue, M. Brown, J. Knowles, H. Wang, D.S. Broomhead, D.B. Kell, *Molecular Biosystems*, 2006, 2, 640.
- [63] K.G. Gadkar, J. Varner, F.J. Doyle III, *Systems Biology*, **2005**, *2*, 1, 17.
- [64] S. Srinath, R. Gunawan, *Journal of Biotechnology*, **2010**, *149*, 132.
- [65] S. Wu, T.J. Harris, K.B. McAuley, *The Canadian Journal of Chemical Engineering*, **2011**, *89*, 148.
- [66] L.T. Biegler, J.J. Damiano, G.E. Blau, *American Institute of Chemical Engineers Journal*, **1986**, *32*, 1, 29.
- [67] S. Wu, K. McLean, T.J. Harris, K.B. McAuley, *International Journal of Advanced Mechatronic Systems*, revisions submitted 2010.
- [68] M. Wulkow, *Macromolecular Reaction Engineering*, **2008**, *2*, 6, 461.
- [69] M. Schwaab, J.C. Pinto, *Chemical Engineering Science*, **2007**, *62*, 2750.
- [70] M. Schwaab, L.P. Lemos, J.C. Pinto, *Chemical Engineering Science*, **2008**, *63*, 2895.
- [71] D.G. Watts, *Canadian Journal of Chemical Engineering*, **1994**, *72*, 4, 701.
- [72] D.J. Pritchard, D.W. Bacon, *Chemical Engineering Science*, **1978**, *33*, 1539.
- [73] S.K. Soh, D.C. Sundberg, *Journal of Polymer Science: Polymer Chemistry Edition*, **1984**, 20, 1315.

Chapter 3 – Modeling the Chemically Initiated Polymerization of Styrene

3.1 Abstract

A styrene polymerization model incorporating industrially-relevant dicumyl peroxide and biphenyl peroxide initiation as well as thermal initiation is developed. Peroxide-induced mid-chain scission is also considered as it may significantly affect the molecular weight of the polystyrene product under some experimental conditions. It is shown that the assumption of zero initial adduct concentration results in poor predictions and that better results are obtained if the initial adduct concentration is calculated using the stationarystate hypothesis. Using initial parameter values from the literature^[1, 2, 3], parameter ranking, selection and estimation techniques are used to refine model predictions. Several attempts at parameter estimation are performed to improve fits to conversion and molecular weight data from the literature. Key model parameters are also tuned manually to improve trends in model predictions. Sensitivity analysis shows improved model predictions of the available literature data when mid-chain scission reactions are ignored, and when chain transfer to monomer is considered along with chain transfer to adduct. After estimation of the 9 most-estimable parameters the value of the weighted nonlinear least squares objective function is 73 % lower than the value obtained using initial literature parameter values. In the future, with additional experimental data, it should be possible to obtain improved parameter estimates and model predictions.

3.2 Introduction

Mathematical models describing polymerization processes are useful tools for process design and for selection of operating conditions to achieve desired product properties. Models for industrial use should accurately predict molecular weight behaviour and the time required to reach the desired conversion at different operating conditions of industrial interest. For example, polystyrene (PS) is synthesized commercially using suspension polymerization at moderate temperatures (60 – 150 °C) and near-atmospheric pressures in large batch reactors.^[4] Due to current knowledge about polymerization mechanisms and autoacceleration phenomena, PS models are often complicated and contain numerous model parameters. Although mathematical models for PS production have existed for many years^[5-12], developing models that provide a good quantitative match to molecular weight distribution (MWD), molecular weight average and conversion data collected over the range of industrial operating conditions is still a challenge.

In this chapter, focus is on chemically initiated styrene polymerization in bulk or suspension using two industrially important peroxide initiators: dicumyl peroxide (DCP) and benzoyl peroxide (BPO). These initiator molecules are symmetrical and fragment into two identical radical species upon thermal decomposition, as indicated by Reaction 1 and 2 in Table 3.1. The fragmentation reaction for BPO is shown in Figure 3.1. Since the initiator fragments are much more soluble in styrene than water, suspension polymerization using these monomers can be modeled in the same fashion as bulk polymerization.^[13, 14] Several authors have developed models to describe styrene polymerization in bulk or suspension and have estimated the associated rate coefficients.^[7, 15-20] Different research groups have provided a variety of estimates for rate coefficients and activation energies for DCP and BPO decomposition, as shown in Table 3.2. Note that reported values for k_{dBPO} vary by a factor of 10 at 100 °C using the parameters in Table 3.2.



Figure 3.1 – Thermal decomposition of a BPO initiator to two primary radicals.

Reaction Type	Reaction	Number
DCP Decomposition	$\text{DCP} \xrightarrow{k_{\text{dDCP}}} 2 f_1 P_{0\text{DCP}}^*$	1
BPO Decomposition	$BPO \xrightarrow{k_{dBPO}} 2 f_2 P_{0BPO}^*$	2
DCP Initiation	$P_{0DCP}^* + M \xrightarrow{k_{iDCP}} P_1$	3
BPO Initiation	$P_{0BPO}^{*} + M \xrightarrow{k_{iBPO}} P_{1}$	4
DCP Mid-Chain β-scission	$P_{0DCP}^{*} + D_{n+m} \xrightarrow{k_{sDCP}} D_n + P_m^{*}$	5
BPO Mid-Chain β-scission	$P_{0BPO}^{*} + D_{n+m} \xrightarrow{k_{sBPO}} D_n + P_m^{*}$	6
Adduct Formation	$M + M \xrightarrow[k_{-1}]{k_1} AH$	7
Adduct Radical Formation	$AH + M \xrightarrow{k_i} A^* + M^*$	8
Adduct Initiation	$A^* + M \xrightarrow{\text{fast}} P_1$ $M^* + M \xrightarrow{\text{fast}} P_1$	9 10
Propagation	$P_n + M \xrightarrow{k_p} P_{n+1}$	11
Termination by Combination	$P_n + P_m \xrightarrow{k_{tc}} D_{n+m}$	12
Termination by Disproportionation	$P_n + P_m \xrightarrow{k_{td}} D_n + D_m$	13
Termination by DCP Radical	$P_n + P_{0DCP}^* \xrightarrow{k_{tDCP}} D_n$	14
Termination by BPO Radical	$P_n + P_{0BPO}^* \xrightarrow{k_{tBPO}} D_n$	15
Chain Transfer to Adduct	$P_n + AH \xrightarrow{k_{fd}} D_n + A^*$	16

Table 3.1. Kinetic mechanism for chemically and thermally initiated polymerization of styrene

Table 3.2. Initiator decomposition kinetic parameters (k_{dDCP}, k_{dBPO}) reported by various authors.

Initiator	A (L mol ⁻¹ s ⁻¹)	E _a /R (K)	k _d (T) (L mol ⁻¹ s ⁻¹)	Т (°С)	Ref.
DCP	9.24×10^{15}	1.84×10^4			[15]
DCP	3.06×10^{12}	1.51×10^4			[16]
DCP	5.5×10^{17}	$1.84 \text{x} 10^4$			[7]
DCP		1.69×10^4	8.75x10 ⁻⁵	128	[17]
BPO	6.94×10^{13}	$1.47 \text{x} 10^4$			[15]
BPO	$1.7 \mathrm{x} 10^{15}$	1.51×10^4			[18]
BPO	2.29×10^{14}	1.37×10^4			[19]
BPO	1.44×10^{13}	1.47×10^4			[20]

Reaction 5 and 6 in Table 3.1 account for chain scission reactions involving primary peroxide radicals. A sample mechanism for these reactions is shown in Figure 3.1.These reactions may influence MWD in situations where the reacting mixture is held at a relatively high temperature for long periods of time to ensure nearly complete styrene conversion.^[21] Madras and McCoy studied the kinetics of scission reactions involving ditert-butyl peroxide (DTBP) radicals in PS at 155 °C.^[3] The authors indicate that the elementary reactions involved in this polymer degradation process are as follows:



Figure 3.2 – Peroxide-facilitated mid-chain hydrogen abstraction followed by β -scission.

 $\text{DTBP} \to 2\text{DTBP}^* \tag{3.1}$

 $DTBP^* + D_{n+m} \rightarrow D_{n+m}^*$ (3.2)

$$\mathbf{D}_{n+m}^* \to \mathbf{D}_n + \mathbf{P}_m^*. \tag{3.3}$$

Nevertheless, Madras and McCoy developed an empirical model using the following pseudo reaction:^[3]

$$DTBP + D_{n+m} \xrightarrow{k_{sDTBP}} D_n + P_m^*,$$
(3.4)

and determined that $\kappa_{sDTBP} = (k_{sDTBP}/W) = 1.37 \times 10^{-6} \text{ Lg}^{-1} \text{ s}^{-1}$ at 155 °C, where W is the molecular weight of a chain undergoing scission. Kim and McCoy subsequently determined that the activation energy for the overall reaction (Equation 3.4) is 1.12×10^{1} kJ mol⁻¹.^[22] Xue et al. studied the scission of PS by DCP and determined an overall activation energy of 6.66×10^{1} kJ mol⁻¹.^[23] To my knowledge, rate parameters for elementary Reaction 5 and 6 in Table 3.1 have not been determined experimentally.

At temperatures above ~100 °C, styrene can undergo thermal initiation, as shown in Reaction 7 through 10 in Table 3.1.^[5, 24] In Reaction 7, two styrene molecules react to form an unstable adduct (AH) that can either decompose to regenerate the two styrene molecules or undergo hydrogen-atom transfer with a third styrene molecule to produce primary radicals, M* and AH* (Reaction 8). These radicals initiate free-radical polymerization (Reaction 9 and 10). M* and AH* radicals are usually assumed to have identical rate constants for initiation.^[25-27]

The MWD of PS can be influenced by scission (Reaction 5 and 6), propagation (Reaction 11), termination (Reaction 12 through 15) and chain transfer (Reaction 16). Note that in Chapter 2, termination by primary radicals is not included in the mechanism as it was found that additional termination resulting from these radicals did not result in a discernible effect on model predictions. Two types of chain-transfer reactions have been considered in bulk styrene polymerization models: transfer to monomer and transfer to AH. Some models consider only transfer to monomer^[12, 19], whereas others consider only transfer to adduct^[1, 5] and some consider both^[5, 7, 26] reactions. There are significant

discrepancies in the literature regarding appropriate values of chain-transfer rate coefficients.^[26, 28] AH molecules contain a proton on a tertiary carbon, which is readily abstracted during chain-transfer reactions,^[29] whereas styrene molecules do not contain easily-abstractable protons. As a result, organic chemists believe that transfer to AH is by far the dominant chain-transfer mechanism.^[24, 29] Chain-transfer to monomer is not shown in Table 3.1.

Several experimental studies have been conducted to investigate the kinetics of bulk and suspension styrene polymerization at temperatures between 90 and 170 °C. In the previous chapter's modeling work, a model is fitted to conversion and MWD data obtained by Hui and Hamielec^[5] between 100 and 165 °C as well as conversion data obtained by Korolev et al.^[8] and Kotoulas et al.^[7] at higher temperatures. Unfortunately, conversion data from one experimental run by Hui and Hamielec and several sets of M_n and M_w measurements obtained by Hui and Hamielec and Kotoulas et al. were neglected. Hui and Hamielec's experiments were run in sealed glass test tubes, with no attempt to remove oxygen. Very little information is provided by Kotoulas et al. and Korolev et al. concerning the experimental procedures used in their work. Additional thermal polymerization studies have been conducted at higher temperatures at which chain-end degradation reactions (not included in Table 3.1) become important.^[30, 31]

Villalobos et al.^[19] used BPO initiator at 90 °C to obtain conversion, M_n and M_w data. Their experiments were conducted in small glass ampoules, suspended in a temperaturecontrolled oil bath. Kotoulas et al.^[7] used DCP initiator at temperatures ranging from 120 to 150 °C to obtain conversion, M_n , M_w and MWD data. Additional styrene polymerization data in the literature were obtained using different initiators (e.g., azobisisobutyronitrile (AIBN) and polypropylene/triethylenetetramine)^[32, 33], which are not of interest in the current study. Recently, numerous studies have been conducted using controlled-radical polymerization techniques involving chemical species and reactions that are not shown in Table 3.1^[9, 26, 34-37]

Some of the earliest styrene free-radical modeling work was done by Hamielec et al.^[38] They studied the AIBN-initiated free radical polymerization of styrene between 50 and 75 °C in benzene solution with monomer loadings ranging from 30 to 100 % by weight. In their model, Hamielec et al. used literature values for kinetic parameters and correction factors for solvent effects.^[39-41] They fitted the initiator efficiency factor, f, by hand and obtained reasonably good fits for molecular weight and conversion data at conversions of up to 40 %.^[38] Pryor and Coco^[25] developed one of the first styrene polymerization models that incorporates Reaction 7 through 10 and 16 from Table 3.1. They adjusted the values of parameters k_1 , k_1 , k_i and k_{fd} by hand to obtain plausible values to fit their data obtained using AIBN and BPO initiators at 60 °C. Later, Hui and Hamielec developed a simplified styrene thermal polymerization model.^[5] They followed the initiation mechanism proposed by Mayo^[24] and Pryor and Coco^[25] (Reaction 7 through 10 in Table 3.1), but applied the stationary-state hypothesis to the adduct and assumed an overall third-order reaction for radical generation and fitted the associated rate constant.

Advances in the understanding of the effects of high-viscosity polymerization conditions on kinetic parameters led to several models that account for the gel effect (i.e., autoacceleration behaviour due to diffusion limitations). One popular and successful

approach first used by Marten and Hamielec employs a semi-empirical treatment to describe the free volume in a polymerizing mixture and its effect on rate coefficients.^[42] Over the years, this approach has been extended by several research groups, resulting in the equations shown in Table 3.3. Marten and Hamielec used their original diffusion model to match experimental data from AIBN-initiated polymerization at a relatively low temperature (< 80 °C). Several empirical parameters were estimated to obtain good fits to the data. A more complicated autoacceleration model, involving the direct calculation of diffusion coefficients for each species in the polymerizing mixture, was developed by Chiu et al.^[43] who fit selected parameters to poly(methyl methacrylate) (PMMA) production data. Chiu's model, which has also been used to predict conversion and MWD data for styrene polymerization,^[44, 45] incorporates more parameters and more complex equations than the model shown in Table 3.3. A comparison of the two different diffusion models by Vivaldo-Lima et al.^[6] indicates that Chiu's model may not be appropriate for systems like PS that exhibit subtler autoacceleration behaviour than does PMMA. Marten and Hamielec's model was shown to be accurate and reliable in predicting conversion and average molecular weight data for AIBN-initiated polymerization of styrene between 60 and 90 °C, using Marten and Hamielec's estimated parameter values.^[6]

Equation Ref	. No.	
Additional Equation used in First Stage of Diffusion Control		
$k_{t,seg} = k_{to} (1 + \delta_c C_p MW) $ ^[12]	(3.5)	
Additional Equations used in Second Stage of Diffusion		
(A) [42]		
$K = M_w^2 e^{\sqrt{V_f}}$	(3.6)	
$K_{cr} = A_{cr} e^{\left(\frac{E_{cr}}{RT}\right)} $ ^[42]	(3.7)	
$V_{f} = \sum_{i=1}^{3} \omega_{i} V_{i}^{*} V_{f,i} $ ^[46, 4]	(3.8)	
$V_{f,i} = V_{g,i} + \alpha_i (T - T_{g,i})$ ^[46,4]	(3.9)	
$k_{\rm T} = k_{\rm to} \left(\frac{M_{\rm w,cr}}{M_{\rm w}}\right)^n e^{\left[-A\left(\frac{1}{V_{\rm f}} - \frac{1}{V_{\rm f,cr}}\right)\right]} $ ^[12]	(3.10)	
$k_{t,rd} = k_{t,rd,min}X + k_{t,rd,max}(1 - X)$ ^[48]	(3.11)	
$k_{t,rd,min} = A_{min}k_{p,eff}[M] $ ^[47]	(3.12)	
$k_{t,rd,max} = A_{max}k_{p,eff}[M] $ ^[47]	(3.13)	
$A_{\min} = \frac{4}{3}\pi a^2 \sigma $ ^[49]	(3.14)	
$A_{\rm max} = \frac{8}{3}\pi a^3 j_{\rm c}^{1/2} $ ^[49]	(3.15)	
$k_{t,eff} = \left(\frac{1}{k_{t,seg}} + \frac{1}{k_T}\right)^{-1} + k_{t,rd} $ ^[9]	(3.16)	
Additional Equations used in Third Phase of Diffusion Control		
$V_{\text{form}} = V_{\text{form}} e^{\left(\frac{-E_{\text{crm}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right)} $ [10, 12]	2] (3.17)	
$k_{p,eff} = k_{po} \exp\left[-B\left(\frac{1}{V_f} - \frac{1}{V_{f,crM}}\right)\right]$ ^[42]	(3.18)	
Additional Equation used in Fourth Phase of Diffusion Control		
$C_{\rm rRatio} = \frac{V_{\rm f,creff}}{V_{\rm c}} $ ^[1]	(3.19)	
$f_{i,eff} = f_{0i} \exp\left[-C\left(\frac{1}{V_f} - \frac{1}{V_{f,creff}}\right)\right]$ [10, 1]	2] (3.20)	

Table 3.3. Model equations describing the diffusion control of important kinetic rate coefficients.

Villalobos et al. developed a model describing the synthesis of expandable polystyrene (EPS) using either BPO or bi-functional initiators.^[19] They used Hui and Hamielec's third-order thermal initiation treatment and Marten and Hamielec's autoacceleration model and fitted a polymer solubility parameter along with two autoacceleration parameters. No information was provided concerning how these parameters were chosen for fitting, or why all other parameters used in their model were left at their literature values. Villalobos et al. obtained good fits to their conversion and molecular weight data.

Prior to the mid-1990s, modelers relied on propagation and termination rate coefficient values determined by fitting conversion and molecular weight data or from the rotating sector method, which produces imprecise estimates.^[39, 41, 50-53] More recently, improved experimental techniques have been developed and are used to more-accurately determine rate coefficient values for propagation and termination. Pulsed-laser polymerization coupled with gel-permeation chromatography has become the *de facto* experimental method for determination of these important rate coefficients and has been used to obtain reliable values for styrene polymerization.^[53-57] Several styrene polymerization models have incorporated these rate coefficients and have obtained good fits to experimental data.^[26, 27, 30, 31, 58] Unfortunately, reliable values for other kinetic rate parameters are still not always available.

To my knowledge, Kotoulas et al. have developed the only model shown to accurately predict data from both chemically initiated and purely thermally initiated styrene polymerization experiments.^[7] Their model includes the full thermal initiation mechanism in Table 3.1 and employs the autoacceleration treatment of Chiu et al.^[43]. Their k_p and k_t

values (2.56x10² L mol⁻¹ s⁻¹ and 9.95x10⁷ L mol⁻¹ s⁻¹ respectively) were obtained from model fitting studies^[25, 28, 47, 50, 59] rather than from PLP studies, which give higher values for both $(3.43 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1} \text{ and } 1.11 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \text{ respectively})$.^[54, 55] No information is provided about how Kotoulas et al. determined which parameters to estimate and which to leave at literature values. Subsequently, Penlidis and co-workers^[10-12, 60, 61] developed a series of detailed styrene polymerization models using k_p and k_{tc} values obtained from PLP studies. In a recent article^[12], they used the autoacceleration model shown in Table 3.3 to account for diffusion effects on kinetic coefficients. They used non-linear regression to estimate the free-volume at which initiation becomes diffusion controlled, the initiator-specific empirical parameter, C, which dictates the strength of the diffusion effect, and the empirical parameter, A, which is also initiator-dependent.^[60] In a subsequent article^[61], they discuss their efforts to obtain rate coefficients k_1 and k_i (used in Reaction 7 and 8) based on experimental results from Zhang and Ray^[18], and Bonilla et al.^[36] Note that Belincanta-Ximenes et al.^[61] do not consider an adduct decomposition reaction (reverse Reaction 7 in Table 3.1) in their model, which is considered in other PS models [7, 25, 26, 28]

In the previous chapter, a mathematical model describing the thermally-initiated polymerization of styrene is presented and the literature on the kinetics of thermal initiation is reviewed. Propagation and termination parameters for the model were obtained from pulsed-laser-polymerization (PLP) studies.^[54, 55] The autoacceleration equations in Table 3.3 were used to account for the influence of increasing viscosity on kinetic coefficients. Statistical techniques^[62-66] were used to select four key parameters for estimation (i.e. k_{fdo} at 120 °C, and the activation energies for transfer to adduct, adduct

decomposition and adduct initiation) because these parameters had a large influence on model predictions and had large uncertainties (e.g., previous literature values for k_{fdo} vary from 50 - 700 L mol⁻¹ s⁻¹ at 120 °C).^[25, 26] Experimental conversion and MWD data from Hui and Hamielec^[5], and conversion data from Korolev et al.^[8] and Kotoulas et al.^[7] were used to estimate the four parameters, resulting in good fits to the data. Two autoacceleration parameters were adjusted by hand to ensure that the onset of autoacceleration occurred at the correct conversion.^[1] It is unclear whether the parameter values that were estimated will provide good predictions in models that involve chemical initiators.

In summary, although many successful models have been developed to describe styrene polymerization, values for some parameters are still uncertain and there are large disparities between reported values of kinetic coefficients fitted using different sets of experimental data. Many modelers have focused only on prediction of data obtained from their own experiments. When attempting to fit their experimental data, modelers have had difficulty deciding which parameters to estimate and which to leave at literature values from previous kinetic studies involving PS. In the current article, a PS model is developed that can describe available conversion and molecular weight data for chemically and thermally initiated polymerization in the industrial temperature range from 90 to 170 °C. Because some literature data for conversion, M_n and M_w were overlooked in Chapter 2, it is first determined whether parameter values from Chapter 2 are able to reliably predict these additional data. Assumptions about the initial adduct concentration and its influence on model predictions are assessed. Updated parameter estimates are obtained in light of the additional thermal polymerization data. Next, the complete set of literature data

(involving initiation with DCP^[7], BPO^[12] or thermal initiation alone^[5, 7]) is used to estimate selected model parameters. Parameters are chosen using statistical techniques^[64, 65] that account for their influence on model predictions, uncertainty in their initial values, and correlated effects with other parameters. Where possible, well-known and unimportant parameters are left at their literature values and only those parameters that will result in a significant improvement in model predictions are adjusted.^[62, 63, 66] The model fit to the data is assessed and recommendations are made about possible improvements in model predictions, either by obtaining better experimental data for parameter estimation, or by modification to the model structure.

3.3 Model Development and Initial Parameter Values

The model was developed and solved using Predici^{TM[67]}, which generates dynamic species balances using reactions selected from a library containing all of the reactions for the current model (shown in Table 3.1). Predici uses the discrete Galerkin method to solve the balance equations and to predict average molecular weights and MWD. Implementation of the diffusion-controlled kinetic equations (shown in Table 3.3) in Predici and selection of appropriate settings to ensure numerical accuracy are described in Chapter 2 and in Appendix 1. To aid parameter estimation and reduce correlation among parameter estimates, Arrhenius expressions were implemented in the following reparameterized form:^[68, 69]
$$k = k_{ref} e^{\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)}$$
(3.21)

rather than in the traditional form, which uses a pre-exponential factor. The reference temperatures, T_{ref} , for each parameter (shown in Table 3.4) are the experimental temperatures used by the authors who estimated the parameter values. Table 3.4 also shows lower and upper bounds for each parameter, which reflect the uncertainty in the experimental techniques used by researchers who calculated the parameter values.

Par.	Ref. Temp. (°C)	k _{ref}	Lower Bound k _{ref}	Upper Bound k _{ref}	E _a /R (K)	Lower Bound E _a /R	Upper Bound E _a /R	Ref.
k _{dDCP}	130	1.53×10^{-4} s ⁻¹	1.0x10 ⁻⁵	9.2x10 ⁻⁴	$1.84 \text{x} 10^4$	1.0×10^{3}	1.1×10^{5}	[15]
f _{DCP}		0.7	3.0x10 ⁻¹	9.0x10 ⁻¹				[70, 71]
k _{dBPO}	90	1.75x10 ⁻⁴ s ⁻¹	1.0x10 ⁻⁵	1.1x10 ⁻³	$1.47 \text{x} 10^4$	1.0×10^{3}	1.0×10^5	[15]
f _{BPO}		0.7	3.0x10 ⁻¹	9.0x10 ⁻¹				[70, 71]
k _{iDCP}	60	3.44×10^3 L mol ⁻¹ s ⁻¹	2.4×10^3	4.5×10^{3}	3.91×10^3	2.7×10^{3}	5.1×10^{3}	[54]
k _{iBPO}	60	3.44×10^3 L mol ⁻¹ s ⁻¹	2.4×10^3	4.5×10^{3}	3.91x10 ³	2.7×10^{3}	5.1×10^3	[54]
k _{sDCP}	155	6.99×10^{1} L mol ⁻¹ s ⁻¹	0.0	$1.4 \text{x} 10^2$	3.62×10^3	$1.0 \mathrm{x} 10^2$	7.2×10^3	[3, 22]
k _{sBPO}	155	6.99×10^{1} L mol ⁻¹ s ⁻¹	0.0	1.4×10^2	3.62×10^3	$1.0 \mathrm{x} 10^2$	7.2×10^3	[3, 22]
k ₁	101.25	2.27×10^{-9} L mol ⁻¹ s ⁻¹	1.0×10^{-10}	4.5x10 ⁻⁹	1.12×10^4	1.0×10^{3}	$2.7 \text{x} 10^4$	[1, 72]
k_1/k_{-1}	120	4.37×10^{-3}	1.0×10^{3}	1.3×10^{5}	6.49×10^3	$1.0 \mathrm{x} 10^2$	$1.3 \text{x} 10^4$	[1, 7]
ki	160	8.46×10^{-5} L mol ⁻¹ s ⁻¹	1.0x10 ⁻⁶	$1.7 \text{x} 10^{-4}$	1.20×10^4	1.0×10^{-6}	$1.7 \text{x} 10^{-4}$	[1, 7]
f_i		0.7	3.0×10^{-1}	9.0×10^{-1}				[70, 71]
k _p	60	3.44×10^2 L mol ⁻¹ s ⁻¹	2.4×10^2	4.5×10^2	3.91x10 ³	2.7×10^{3}	5.1×10^{3}	[54]
k _{tc}	60	1.11×10^8 L mol ⁻¹ s ⁻¹	*	*	7.53×10^2	*	*	[55]
k _{td}	60	1.59×10^7 L mol ⁻¹ s ⁻¹	*	*	7.53×10^2	*	*	[55]
k _{tDCP}	60	1.11x10 ⁸ L mol ⁻¹ s ⁻¹	*	*	7.53×10^2	*	*	[55]
k _{tBPO}	60	1.11×10^8 L mol ⁻¹ s ⁻¹	*	*	7.53×10^2	*	*	[55]
k _{fd}	60	1.98×10^2 L mol ⁻¹ s ⁻¹	*	*	4.54×10^3	*	*	[1]

Table 3.4. Literature values for kinetic parameters.

* indicates that these parameters were reparameterized before parameter estimation. Associated bounds are provided in Table 3.5.

To further reduce correlation during parameter estimation, the model was formulated in terms of the following composite parameters: k_{tco}/k_{po} , k_{ktdo}/k_{po} , $[(E_a/R)_{tc} - (E_a/R)_p]$ and $[(E_a/R)_{td} - (E_a/R)_p]$ instead of rate coefficients for termination and their activation energies. Similarly, the model was written in terms of composite kinetic parameters

 k_{fdo}/k_{po} and $[(E_a/R)_{fd} - (E_a/R)_p]$, as shown in Table 3.5. Note that the value of 6.9861x10¹ L mol⁻¹ s⁻¹ for k_{sDCP} and k_{sBPO} in Table 3.4 was calculated using experimental results of McCoy and co-workers,^[3, 22] as shown in Appendix 2. The large uncertainty range for these parameters was selected because the initiator used in McCoy's studies was di-tert-butyl peroxide rather than DCP or BPO.

		1	1	
Parameter	Initial Value	Lower Bound	Upper Bound	Refs.
k _{tco} /k _{po}	3.22×10^5	2.3×10^5	4.2×10^5	[54, 55]
$[(E_a/R)_{tc} - (E_a/R)_p]$	-3.16×10^3	-4.1×10^3	-2.2×10^3	[54, 55]
k _{ktdo} /k _{po}	4.61×10^4	3.2×10^4	$6.0 ext{x} 10^4$	[54, 55]
$[(E_a/R)_{td} - (E_a/R)_p]$	-3.16×10^3	-4.1×10^3	-2.2×10^3	[54, 55]
k _{kfdo} /k _{po}	5.77x10 ⁻¹	1.0x10 ⁻²	3.5	[1, 54]
$[(E_{a}/R)_{fd} - (E_{a}/R)_{p}]$	6.32×10^2	0.0	3.8×10^3	[1, 54]

Table 3.5. Initial values and bounds for reparameterized parameters.

In Chapter 2, it is assumed that the kinetic parameters determined via pulsed-laser polymerization (PLP) are known to within 5 %. Uncertainty analysis by PLP researchers ^[54, 55] indicate, however, that k_p and k_t estimates have uncertainties as large as 25 or 30 %. These larger uncertainties are reflected in the bounds shown in Table 3.4. Furthermore, it is believed that uncertainties of 10 and 15 % that were assigned to k_{10} and its activation energy, respectively, were too low in Chapter 2, because it is unrealistic to assume that the methods^[72] used to determine these parameters would provide values that are more reliable than PLP values for k_p and k_t . A more realistic uncertainty range is reflected by the revised bounds in Table 3.4.

Parameter ranking via estimability analysis requires scaling factors that reflect uncertainty in initial parameter values and in measured data.^[5, 7, 19] Scaling factors for the various model parameters were chosen as half the distance between the lower and upper bound

for each parameter. Uncertainties for conversion measurements were set to 2 % of the average of all conversion measurements. Uncertainty scaling factors for M_n and M_w measurements were set at 5 % of the average of all M_n and M_w measurements, respectively. Finally, the uncertainty of measured points on MWD curves was set to 50 % of the average height of all measured points on MWD curves. These uncertainties were selected after examining proprietary replicate industrial styrene polymerization data for conversion and molecular weight.

Equation 3.6 and 3.7 in Table 3.3 govern the onset of diffusion-controlled termination reactions between polymer radicals. Termination of growing polymer chains by peroxide radicals (Reaction 14 and 15 in Table 3.1) will become diffusion controlled later in the polymerization because these reactions involve a long chain and a small molecule, similar to propagation. Therefore, it is assumed that termination by peroxide radical should become diffusion controlled when propagation becomes diffusion controlled (i.e., when V_f falls below $V_{f,crm}$) resulting in the following equation for termination by DCP radicals and a similar equation for BPO radicals:

$$k_{tDCP,eff} = k_{tDCP,ref} \exp\left[-B\left(\frac{1}{V_f} - \frac{1}{V_{f,crM}}\right)\right]$$
(3.22)

Parameters used in diffusion-control equations are shown in Table 3.6 along with their initial values and bounds. Physical constants are shown in Table 3.7 along with definitions for the variables that are calculated from expressions in Table 3.3.

Symbol	Name	Initial	Units	Lower	Upper	Ref.
		Value		Bound	Bound	
а	root-mean-squared end-to- end distance per square root of the number of monomer units	7.5x10 ⁻¹⁰	m num ^{-1/2}	3.8x10 ⁻¹⁰	1.1x10 ⁻⁹	[35]
А	adjustable parameter for the onset of the 2 nd stage of diffusion control	3.48x10 ⁻¹	dimensionless	1.7x10 ⁻¹	5.2x10 ⁻¹	[22]
K _{ref}	adjustable parameter for the onset of the 2 nd stage of diffusion control	350	kg ^{0.5} mol ^{-0.5}	1.8x10 ²	5.3x10 ²	[22]
V _{fcrmo}	adjustable parameter for the onset of the 3 rd stage of diffusion control	3.06x10 ⁻²	dimensionless	1.8x10 ⁻¹	4.3x10 ⁻¹	[22]
В	adjustable parameter for the 3 rd stage of diffusion control	1	dimensionless	0.5	1.0	[22]
C	adjustable parameter for the 4 th of diffusion control (thermal initiation)	1	dimensionless	0.5	1.0	[22]
C ₁	adjustable parameter for the 4 th of diffusion control (DCP initiation)	1	dimensionless	0.5	1.0	
C ₂	adjustable parameter for the 4 th of diffusion control (BPO initiation)	1	dimensionless	0.5	1.0	
E _{cr}	adjustable parameter for the onset of 2^{nd} stage of diffusion control	3.83x10 ³	cal/mol	1.9x10 ³	5.7x10 ³	[22]
E _{crm}	adjustable parameter for the onset of the 3 rd stage of diffusion control	1.67x10 ³	cal/mol	1.0x10 ³	2.3x10 ³	[22]
jc	number of monomer units between entanglements on a polymer chain	175	num	8.8x10 ¹	2.6×10^2	[36, 37]
n	coefficient for translational diffusion limited termination	1.75	dimensionless	1.1	2.5	[22]
C _{rRatio}	adjustable parameter for the onset of diffusion control for thermal initiation	1	dimensionless	0.0	1.0	[1]
C _{rRatioDCP}	adjustable parameter for the onset of diffusion control for DCP initiation	1	dimensionless	0.0	1.0	
C _{rRatioBPO}	adjustable parameter for the onset of diffusion control for BPO initiation	1	dimensionless	0.0	1.0	
V _m *	specific free volume required for one jumping unit of styrene	9.12x10 ⁻¹	dimensionless	4.6x10 ⁻¹	1.4	[8]
V _p *	specific free volume required for one jumping unit of PS	8.25x10 ⁻¹	dimensionless	4.1x10 ⁻¹	1.2	[8]
α _m	thermal expansion coefficient for styrene	1x10 ⁻³	volume/K	5.0x10 ⁻⁴	1.5x10 ⁻³	[22]
α _p	thermal expansion	4.8×10^{-4}	volume/K	2.4×10^{-4}	7.2×10^{-4}	[22]

Table 3.6. Parameters used in diffusion-control equations.

	coefficient for PS					
δ_{c}	segmental diffusion parameter for styrene	1x10 ⁻³	L/g	5.0x10 ⁻⁴	1.5x10 ⁻³	[22]
σ	Lennard-Jones diameter for a styrene molecule	$7.4 \mathrm{x10}^{-10}$	m	3.7x10 ⁻¹⁰	1.1x10 ⁻⁹	[22]

Symbol	Name	Value	Units	Ref.
MW	molecular mass of styrene	0.10415	kg mol ⁻¹	
T _{g,m}	glass transition temperature of styrene	185	K	[22]
T _{g,p}	glass transition temperature of PS	378	K	[22]
V _{g,m}	specific free volume of styrene at its glass transition temperature	2.5x10 ⁻²	dimensionless	[22]
V _{g,p}	specific free volume of PS at its glass transition temperature	2.5x10 ⁻²	dimensionless	[22]
R	universal gas constant	1.9859	cal K ⁻¹ mol ⁻¹	
Т	Temperature		K	
M _w	weight-average molecular weight of dead polymer chains		kg mol ⁻¹	
K	critical variable for the onset of the 1 st stage of diffusion control		kg ^{0.5} mol ^{-0.5}	
K _{cr}	critical constant for the onset of the 1 st stage of diffusion control		$kg^{0.5} mol^{-0.5}$	
$V_{\rm f}$	total system free volume		dimensionless	
V _{f,m}	fractional free volume of styrene in the system		dimensionless	
$V_{f,p}$	fractional free volume of PS in the system		dimensionless	
V _{fcr}	free volume at the onset point of the 1 st stage of diffusion control		dimensionless	
M _{wcr}	weight-average molecular weight of dead polymer chains at the onset point of the 1 st stage of diffusion control		kg mol ⁻¹	
ωm	weight fraction of styrene in the system		dimensionless	
ω _n	weight fraction of PS in the system		dimensionless	
X	fractional conversion of styrene		dimensionless	
[M]	concentration of styrene in the system		mol L ⁻¹	
C _p	concentration of polymer in the system		mol L ⁻¹	
k _{t,seg}	effective-segmental diffusion-limited termination rate coefficient		L mol ⁻¹ s ⁻¹	
k _T	effective translational diffusion-limited termination rate coefficient		L mol ⁻¹ s ⁻¹	
k _{t,rd}	effective reactional diffusion-limited termination rate coefficient		L mol ⁻¹ s ⁻¹	
k _{t,eff}	effective overall diffusion-limited termination rate coefficient		$L \text{ mol}^{-1} \text{ s}^{-1}$	
k _{p,eff}	effective diffusion-limited propagation rate coefficient		L mol ⁻¹ s ⁻¹	
k _{tDCP,eff}	effective diffusion-limited termination-by-DCP- radical rate coefficient		L mol ⁻¹ s ⁻¹	
k _{tBPO,eff}	effective diffusion-limited termination-by-BPO- radical rate coefficient		L mol ⁻¹ s ⁻¹	
V _{fcr,m}	free volume at the onset point of the 2 nd stage of diffusion control		dimensionless	
\mathbf{f}_{i}	efficiency factor for thermally induced radical initiation		dimensionless	

Table 3.7. Calculated variables and physical constants.

3.4 Simulation Results and Parameter Estimation

3.4.1 Predictions of Thermal Polymerization Data

Simulations using parameter values estimated in Chapter 2 (shown in Table 3.4) were performed to assess the quality of model predictions for the additional conversion, M_n and M_w data obtained by Hui and Hamielec^[5] and additional M_n and M_w data from Kotoulas et al.^[7] These new data were not used to fit the parameters in Table 3.4. Figure 3.1 shows the predictions for conversion, M_n and M_w corresponding to the additional data provided by Hui and Hamielec.^[1]



Figure 3.3. Comparisons between experimental conversion (\diamond), M_n (\diamond), and M_w (\Box) data and model predictions (conversion and M_n , —; M_w , ---) using parameter values estimated by Woloszyn and McAuley.^[1] Data are from bulk, thermally-initiated styrene polymerization experiments at 120 °C that were not used in parameter estimation.^[5] The initial adduct concentration was assumed to be 0 mol L⁻¹.

Predictions for the conversion data in Figure 3.1(a) are good but the M_n and M_w predictions are poor. Similarly poor predictions (shown in Figure A.3.1 in Appendix 3) were obtained for the M_n and M_w data of Kotoulas et al.^[7] The predicted high molecular weight at the beginning of the simulations is caused by the production of very long chains in the first few seconds of the simulation (e.g., for the simulation in Figure 3.1, the

predicted instantaneous M_n of polymer chains produced at t = 0.1 seconds is 1.69×10^9 g mol⁻¹ and the corresponding instantaneous M_w of polymer chains is 2.77×10^9 g mol⁻¹). These very long chains have a large effect on cumulative average molecular weights for the first 15000 seconds of the simulation (approximately 4.2 hours). The production of long chains is caused by very low rates of termination and chain transfer in the early stages of the simulation. Termination is slow because of the initially low concentration of radicals. Note that implementation of a chain-transfer-to-monomer reaction helped shift the entire average molecular weight curves downwards, particularly in the first half of the polymerization, when monomer is abundant. However, transfer to monomer could not prevent the very large instantaneous average molecular weights shown in Figure 3.3. Chain transfer to adduct is slow because it had been assumed that the initial adduct concentration is zero. After considering the poor prediction in Figure 3.1(b), it is clear that the assumption of zero initial adduct concentration is not justifiable as some adduct would have formed in the styrene prior to t = 0 in the simulation.

3.4.2 Stationary-State Hypothesis for Initial Adduct Concentration

To ensure that some adduct is present at the start of each simulation, the stationary-state hypothesis (SSH) was implemented for the initial adduct concentration. Reaction 7, 8 and 16 in Table 3.1, influence [AH]_o, so that the initial adduct concentration is:

$$[AH]_{o} = \frac{k_{1}[M]^{2}}{k_{-1} + k_{i}[M] + k_{fd}[P]}$$
(3.23)

The values of the rate coefficients, k_1 , k_{-1} , k_i and k_{fd} are those corresponding to the reaction temperature for the particular recipe. After time zero, the adduct concentration

was computed by PrediciTM using the reaction kinetics shown in Table 3.4. Similar results are obtained if the SSH on adduct is assumed throughout the entire simulation. After implementation of the SSH on initial adduct concentration, the instantaneous M_n and M_w at t = 0.1 seconds decreased to more-reasonable values of 1.25×10^4 g mol⁻¹ and 2.10×10^4 g mol⁻¹, respectively. The conversion and molecular weight predictions were quite poor (see Figure A.3.2 in Appendix 3), indicating that better parameter estimates could result in appreciable improvements in model predictions.

3.4.3 Parameter Ranking and Estimation Using All Thermal Polymerization Data

Parameter selection^[62-65] and estimation were performed with the new assumption concerning [AH]_o. Table 3.8 shows the top-ten ranked parameters and the results of the parameter estimation. Wu's parameter selection method^[62] indicates that the six top-ranked parameters should be estimated, whereas only four parameters were estimated using conversion and MWD data in Chapter 2. The larger data set used in the current study provides more information about appropriate parameter values. These estimated parameter values resulted in a large (97.3 %) decrease in the value of the weighted non-linear least-squares objective function^[1], from 565310 (obtained using the parameter values in Table 3.4, Table 3.5 and Table 3.6) to 15490.

Figure 3.2 shows comparisons of the updated model predictions to the data from Figure 3.1. Note the more-reasonable M_n and M_w behaviour near the beginning of the simulation. Predictions for the full set thermal polymerization data are provide in Figure A.3.3 in Appendix 3.

Rank	Parameter	Initial Value	Lower Bound	Upper Bound	Estimated Value	
1	k_{fdo}/k_{po}	5.77x10 ⁻¹	1.0x10 ⁻²	3.5	6.71x10 ⁻¹	
2	$(E_a/R)_1$	1.12×10^4	1.0×10^{3}	$2.2x10^4$	$1.37 \text{x} 10^4$	
3	$(E_a/R)_i$	$1.20 \mathrm{x} 10^4$	1.0×10^{3}	2.4×10^4	$1.12 \mathrm{x} 10^4$	
4	$(E_a/R)_{1/-1}$	6.49×10^3	1.3×10^4	1.3×10^4	6.46×10^3	
5	$[(E_a/R)_{fd}-(E_a/R)_p]$	6.32×10^2	0.0	3.8×10^3	4.58×10^2	
6	k ₁₀	2.27x10 ⁻⁹	1.0×10^{-10}	4.5x10 ⁻⁹	3.19x10 ⁻¹⁰	
7	E _{cr}	5.00×10^3	2.5×10^3	7.5×10^3		
8	А	3.48x10 ⁻¹	1.7x10 ⁻¹	5.2x10 ⁻¹		
9	k _{io}	8.46x10 ⁻⁵	1.0x10 ⁻⁶	1.7x10 ⁻⁴		
10	α _m	1.00x10 ⁻³	5.0x10 ⁻⁴	1.5x10 ⁻³		

Table 3.8. Ranked parameter list with parameter estimates after implementation of SSH on initial adduct concentration. Initial values were taken from Chapter 2.



Figure 3.4. Comparisons between experimental conversion (\Diamond), M_n (\Diamond), and M_w (\Box) data and model predictions using updated estimated parameter values (—, ---). Data are from bulk, thermally-initiated styrene polymerization experiments at 120 °C.^[5]

3.4.4 Parameter Ranking and Estimation Using Thermally and Chemically

Initiated Polymerization Data

After good predictions of the thermally initiated styrene polymerization data were obtained, parameter ranking and estimation were performed using a larger data set incorporating DCP^[7] and BPO^[19] initiated polymerization data along with thermal polymerization data.^[5, 7] Again, initial values and upper and lower bounds for each parameter are shown in Table 3.4, 3.5 and 3.6. The results of this estimation are shown in

the last column of Table 3.9. Note how the ten top-ranked parameters change with the inclusion of additional data and chemical mechanisms. Figure 3.3 shows representative results for chemically initiated data after estimation of the top five parameters shown in Table 3.9.

morature data.					
Rank	Parameter	Estimated Value			
1	k _{DCPo}	5.00x10 ⁻⁵			
2	k_{fdo}/k_{po}	8.84x10 ⁻¹			
3	$(E_a/R)_{dDCP}$	1.68x10 ⁴			
4	$(E_a/R)_1$	1.33×10^4			
5	$(E_a/R)_i$	1.08x10 ⁴			
6	k ₁₀				
7	$\mathbf{V}_{\mathrm{fmj}}$				
8	k _{BPOo}				
9	α_{m}				
10	E _{cr}				

Table 3.9. Ranked parameter list with parameter estimates fitted against full set of literature data.



Figure 3.5. Comparisons between experimental conversion (\diamond), M_n (\diamond), and M_w (\Box) data and model predictions (—, ---) obtained using parameter values from the first attempt at estimation using thermally and chemically initiated polymerization data. (a, b) Selected thermal polymerization data at 160 °C^[7]; (c, d) Selected DCP-initiated polymerization data at 130 °C, (4000 ppm DCP)^[7]; (d, e) Selected BPO-initiated polymerization data at 90 °C, (3050 ppm BPO)^[19].

The parameter estimation resulted in a 78.9 % improvement in the value of the objective function, which decreased from 160400 to 46819. There were, however, some problems with the general trends, especially for chemically-initiated-polymerization predictions: molecular weight averages were still too high in the early stages of polymerization, although final molecular weights were fairly good. Final conversions were reasonable, although autoacceleration appeared to be triggering too late for predictions of the DCP-

initiated experimental data, and too early for the BPO experiments. Note the large increase in the slope of the conversion curve in Figure 3.3(e) at t = 18000 s followed by an rapid levelling off. This abrupt behaviour is caused by the sharp decrease in the rate of propagation at the onset of the third stage of autoacceleration. Immediately after the available free volume in the system falls below the critical free volume, $V_{fcr,m}$, $k_{p,eff}$ drops by nearly an order of magnitude, and the rate of polymerization decreases accordingly. It is important to note that the drop in the rate of polymerization is not solely caused by monomer starvation, as the maximum conversion achieved is approximately 97 %.

3.4.5 Model Adjustment via Hand Tuning of Important Parameters

Several attempts were made to further decrease the mismatch between model predictions and experimental data. To this end, several influential parameter values were tuned by hand. A comprehensive description of these hand tuning efforts and subsequent parameter re-estimations to find a better local minimum is presented in Appendix 3, and is summarized below. Parameters governing the rate of chemical initiation (k_{dDCPo} , (E_a/R)_{dDCP} and k_{dBPOo}), the strength and onset time for autoacceleration (A and K_{ref}) and transfer to adduct (k_{fdo}/k_{po}) were identified as influential to the shape of the conversion vs. time curves and for trends in the average molecular weights. Fortunately, each parameter chosen for hand tuning had a reasonably distinct effect on model predictions, and so could be tuned independently. Figure 3.4 shows representative predictions using handtuned parameter values shown in Table 3.10. Note that values for the remaining parameter used for the simulations in Figure 3.4 are estimated values from the last column of Table 3.8, or are shown in Table 3.4, 3.5 and 3.6.

Parameter	Initial Value	Hand-Tuned Value	Units
k_{fdo}/k_{po}	6.73×10^{-1}	1.5	dimensionless
k _{dDCPo}	1.53×10^{-4}	1.11×10^{-4}	$L \text{ mol}^{-1} \text{ s}^{-1}$
$(E_a/R)_{dDCP}$	$1.84 \mathrm{x} 10^4$	$1.74 \mathrm{x} 10^4$	K
k_{dBPOo}	1.75×10^{-4}	3.1x10 ⁻⁵	$L \text{ mol}^{-1} \text{ s}^{-1}$
А	3.48×10^{-1}	5.0x10 ⁻¹	dimensionless
K _{ref}	5.0×10^2	2.75×10^2	kg ^{0.5} mol ^{-0.5}

Table 3.10. Values of hand-tuned parameters that were adjusted to improve trends in conversion and molecular weight predictions



Figure 3.6. Comparisons between experimental conversion (\diamond), M_n (\diamond), and M_w (\Box) data and model predictions (—, ---) obtained using hand-tuned parameter values shown in Table 3.10. (a, b) Selected thermal polymerization data at 160 °C^[7]; (c, d) Selected DCP-initiated polymerization data at 130 °C, (4000 ppm DCP)^[7]; (d, e) Selected BPO-initiated polymerization data at 90 °C, (3050 ppm BPO)^[19].

After hand tuning, the initial polymerization rates and the onset times for autoacceleration, shown in Figure 3.4(c and e) are better than those shown in Figure 3.3(c and e). Also, the trends in molecular weight averages after hand tuning, shown in Figure 3.4(b, d, f) are improved. Subsequent parameter ranking and estimation was performed using the newly-hand-tuned parameter values as initial guesses. Unfortunately, the resulting objective function value was 47764, which is slightly higher than 46819 (the value corresponding to the predictions in Figure 3.3), indicating that the new optimum is a local minimum. Simulated M_n and M_w decrease after the onset of autoacceleration, similar to the results shown in Figure 3.3(d and f). This decrease is due to the mid-chain scission reactions (Reaction 5 and 6 in Table 3.1) which cleave polymer chains in the presence of peroxide radicals. The data (except perhaps M_n in Figure 3.3(d)) do not exhibit such reductions in average molecular weight at the end of the polymerizations, and so the values of the mid-chain scission rate coefficients may be too high. In addition, after fitting, the predicted M_n and M_w values at low simulation times tend to be too low for the thermally initiated experiments and too high for the BPO initiated experimental data. Further hand tuning of initial parameter values was attempted to address these concerns in an attempt to find a better minimum for the objective function.

3.4.6 Hand Tuning of Mid-Chain Scission Kinetic Parameters

The initial values of the parameters responsible for mid-chain scission (k_{sDCPo} and k_{sBPOo}) were set to 0 L mol⁻¹ s⁻¹ to determine if a better fit to the data could be obtained by turning off the mid-chain scission reactions. Other parameters were set at their hand-tuned values in Table 3.10. The subsequent parameter ranking and estimation resulted in an objective function value of 38840, the lowest value obtained thus far. The estimated

parameter values are shown Appendix 3 (Table A.3.5) and the full set of model comparisons is shown in Figure A.3.10. Note that there are still some discrepancies in predictions of initial molecular weight when these parameter values are used for model predictions. One mechanism capable of influencing these molecular weights is transfer to monomer, which has been used by numerous authors to help fit their models to experimental data.^[5, 7, 11, 12, 26, 61]

3.4.7 Implementation of Transfer-to-Monomer Reaction

The following transfer-to-monomer reaction was implemented:

$$P_n + M \xrightarrow{\kappa_{fm}} D_n + M^*$$
(3.24)

Initial values of $k_{fmo} = 2.0856 \times 10^{-1} \text{ L mol}^{-1} \text{ s}^{-1}$ at 120 °C and $(E_a/R)_{fm} = 6.377 \times 10^3 \text{ K}$ were computed using the corresponding rate coefficients estimated by Hui and Hamielec.^[1] Parameter ranking and estimation was then performed resulting in J = 34560, the lowest objective function value obtained in this study. Figure 3.5 shows the corresponding representative model predictions. Table 3.11 shows the final estimated parameter values. The values in **bold** were estimated in this parameter estimation attempt. 95 % confidence intervals were calculated for the nine parameters estimated using the procedure shown in Appendix A.1.11. It is important to note that the confidence intervals shown in Table 3.11 are based on the values of all of the fixed parameters used in the model and are may be too narrow. In addition, calculation of the Jacobian matrix requires linearization of the model with respect to the parameters, which may result in poor estimates of the confidence intervals. For these reasons, the confidence intervals reported in Table 3.11 should only be taken as a rough guide. Note that the confidence intervals for k_{dDCPo} , $[(E_a/R)_{fd}-(E_a/R)_p]$, k_{dDCPo} and $(E_a/R)_{DCP}$ contain zero, and therefore should be bounded at zero. The upper bounds give an idea of the uncertainty in the estimates. With the exception of these zero-bounded parameter estimates, all confidence intervals fall within the bounds used for parameter estimation.

Note that the two kinetic parameters for the transfer-to-monomer reaction (k_{fmo} and $(E_a/R)_{fm}$) had only a small influence on model predictions, were ranked 23rd and 13th, respectively and were not subsequently chosen for estimation using Wu's parameter selection algorithm.

Table 3.11. Ranked list of parameters after reduction of mid-chain scission reactions and implementation of transfer-to-monomer reaction using estimated parameter values from Section 3.4.4 as initial guesses and results of parameter estimation. Note that values shown in **bold** were estimated in this attempt.

Rank	Parameter	Final Estimated Value with 95 % Confidence
		Intervals
1	k _{dBPOo}	$4.75 \text{x} 10^{-5} \pm 2.02 \text{x} 10^{-4}$
2	k _{fdo} /k _{po}	$8.25 \text{x} 10^{-1} \pm 1.80 \text{x} 10^{-1}$
3	$[(E_a/R)_{fd}-(E_a/R)_p]$	$3.58 \text{x} 10^2 \pm 1.38 \text{x} 10^3$
4	$(E_a/R)_i$	$9.58 \text{x} 10^3 \pm 1.06 \text{x} 10^3$
5	$(E_a/R)_1$	$1.24 \mathrm{x} 10^4 \pm 8.12 \mathrm{x} 10^2$
6	А	$5.06 \text{ x} 10^{-1} \pm 3.06 \text{ x} 10^{-2}$
7	k _{dDCPo}	$8.68 \times 10^{-5} \pm 9.91 \times 10^{-5}$
8	$(E_a/R)_{dDCP}$	$1.27 \mathrm{x10^4} \pm 1.46 \mathrm{x10^4}$
9	V_{fmj}	$9.99 \text{ x} 10^{-1} \pm 2.60 \text{ x} 10^{-1}$
10	α _m	1.00×10^{-3}
11	α _p	4.80×10^{-4}
12	k ₁₀	3.19x10 ⁻¹⁰
13	$(E_a/R)_{fm}$	6.38×10^3
14	$(E_a/R)_p$	3.91×10^3
15	$(E_a/R)_{1/-1}$	6.46×10^3
16	k _{po}	3.44×10^2
17	$[(E_a/R)_{tc}-(E_a/R)_p]$	-3.16×10^3
18	k _{io}	8.46x10 ⁻⁵
19	k _{tco} /k _{po}	3.21×10^5
20	K _{ref}	9.50×10^2
21	V _{fcrmo}	3.06x10 ⁻²
22	$V_{\rm fpj}$	8.35x10 ⁻¹
23	k _{fmo}	2.09x10 ⁻¹
24	f_{1o}	7.00x10 ⁻¹
25	f ₂₀	7.00x10 ⁻¹
26	f _{io}	7.00x10 ⁻¹
27	n	1.75
28	В	1.00
29	δ _c	1.00×10^{-3}
30	A _{1/-1}	$6.40 \mathrm{x} 10^4$
31	E _{crm}	1.67×10^3



Figure 3.7. Comparisons between experimental conversion (\diamond), M_n (\diamond), and M_w (\Box) data and model predictions (—, ---) obtained using parameter values estimated using thermally and chemically initiated polymerization data after reduction of mid-chain scission reactions and implementation of transfer-to-monomer reaction. (a, b) Selected thermal polymerization data at 160 °C^[7]; (c, d) Selected DCP-initiated polymerization data at 130 °C, (4000 ppm DCP)^[7]; (d, e) Selected BPO-initiated polymerization data at 90 °C, (3050 ppm BPO)^[19].

Predictions of conversion curves are reasonably accurate for thermally and chemically initiated polymerization data, as are predictions for the final conversions. However, there are still some issues with the average molecular weight predictions. For the data shown in Figure 3.5 and the additional data used for parameter estimation, shown in Appendix 3, the molecular weight trends are good for the thermally initiated experiments, but the

predicted initial molecular weights are still too high for the DCP-initiated experimental data. Note that the model predicts a slight decrease in M_n and M_w at high reaction times in Figure 3.5(d and f) even though the mid-chain-scission reactions are turned off.

3.4.8 Importance of Chain-Scission and Transfer-to-Monomer Reactions

It is important to determine whether the improvement in the objective function is primarily due to new initial parameter values, which resulted in a better local minimum, or to the mechanistic changes (i.e., turning off chain scission and including chain transfer to monomer). New simulations were run with the mechanistic changes reversed. First, predictions of the experimental data were generated with k_{sDCPo} and k_{sBPOo} set to their original values (shown in Table 3.4). All other parameter values remained at their estimated values, shown in Table 3.11. The objective function value increased from 34560 to 46967. Similarly, after turning off the transfer-to-monomer reaction with all other parameters set at the values shown in Table 3.11, the objective function value increased from 34560 to 68750. Note that at 50 % conversion, using $k_{fmo} = 2.09 \times 10^{-1} L$ mol⁻¹ s⁻¹, chain transfer to monomer accounts for between 25 and 35 % of the overall chain transfer processes for the simulations shown in Figure 3.5, with the remainder being chain transfer to adduct. These results indicate that the improvement in the model fit to the data can be attributed to the revised mechanistic assumptions as well as updated parameter values. Although the parameter selection algorithm did not choose k_{sDCPo} , k_{sBPOo} or k_{fmo} for estimation, the values of these parameters have an important influence on the quality of the model fit.

To determine how strongly nonlinearity in the model parameters affected parameter ranking, and therefore selection, estimability ranking was performed one final time using the estimated parameter values shown in the last column of Table 3.11. The five top-ranked parameters remained the same, while A and V_{fmj} moved further down the list and α_m and k_{io} moved closer to the top of the list. k_{fmo} moved from 23rd rank to 20th rank, and k_{sDCPo} and k_{sBPOo} remained unranked, i.e., at the bottom of the list. These changes in the ranked list do not significantly change the subset of parameters that are chosen for estimation, and therefore indicate that nonlinearity in the parameters had only a minor influence in the parameter ranking and subset selection.

3.5 Conclusions and Recommendations

A model describing the thermally and chemically initiated polymerization of styrene at industrially relevant temperatures (90 to 170 °C) was developed. It was shown that the assumption of zero initial adduct concentration gives poor model predictions of molecular weight data collected near the start of the experiments. Using the stationary-state hypothesis to calculate the initial adduct concentration resulted in much better predictions of molecular weight data. Since there was insufficient information in the data from thermal initiation experiments to warrant estimation of all 40 model parameters, a subset of the 6 most estimable parameters was selected for estimation. The 6 parameter selected were related to chain transfer to adduct, adduct formation, radical formation from adduct and adduct decomposition to monomers. The improved parameter values reduced the weighted nonlinear least-squares objective function by ~ 97 % indicating a substantial improvement in fit to the thermal polymerization data.

To obtain accurate predictions of conversion and molecular weight literature data from experiments using dicumyl peroxide or biphenyl peroxide initiators, several parameter estimation attempts were made. Five parameters were initially selected for estimation using the algorithm of Wu et al.^[62, 63], reducing the value of the objective function by 71 %. Unfortunately, the estimated parameter values resulted in undesirable trends in some conversion and average molecular weight predictions indicating the likelihood of a local minimum. Six parameters related to the rates of chemical initiation, chain transfer to adduct and the onset point and strength of the second stage of autoacceleration were selected for manual tuning to improve these undesirable trends. In addition, the importance of peroxide-induced mid-chain scission and chain transfer to monomer were investigated by manual parameter adjustments.

Finally, starting from the new initial values, nine parameters (k_{dBPOo} , k_{fdo}/k_{po} , [(E_a/R)_{fd}-(E_a/R)_p], (E_a/R)_i, (E_a/R)₁, A, k_{dDCPo} , (E_a/R)_{dDCP} and V_{fmj}) were selected for estimation, resulting in an improvement of 73 % in the objective function compared to prediction generated using literature values. The selected parameters govern rates of initiation by DCP, BPO and adduct, chain transfer to adduct, and onset points and severity of autoacceleration. Using these final parameter estimates, good fits to conversion, and molecular weight data were obtained except for some mismatch in predictions of initial average molecular weights for some runs. Although the mid-chain scission rate coefficients and chain-transfer-to-monomer rate coefficient were not selected for

estimation by the automated algorithm, simulations reveal that these parameters may have an important influence on molecular weight predictions. Obtaining reliable values for these parameters will require additional experimental data.

The next stage of this work is to apply the model to prediction of a large set of proprietary industrial data. It is possible that consideration of a large amount of data will result in more parameters selected for estimation and therefore better predictions of conversion and molecular weight. At this stage, use of these estimated parameter values shown in Table 3.11 and all remaining parameter values shown in Table 3.4, 3.5 and 3.6 is recommended when making predictions for thermally initiated and chemically initiated styrene polymerization data.

The parameter ranking algorithm developed by Yao et al.^[65] and Thompson et al.^[64] and the parameter selection technique of Wu et al.^[62, 63], greatly simplified the parameter estimation process. Using these techniques, the most influential and uncertain parameters were selected for estimation. Unimportant and already-well-known parameters were held at their initial literature values. As a result, numerical problems and parameter value runaway toward unrealistic values were avoided during parameter estimation. Because of these estimation tools, effort could be directed towards examination of subtle trends in model predictions and use of engineering and scientific judgement to hand-tune parameter values to improve these trends.

3.6 References

- [1] J.D. Woloszyn, K.B. McAuley, *Macromolecular Reaction Engineering*, **2011**, *5*, 9-10, 453.
- [2] B.J. McCoy, M. Wang, *Chemical Engineering Science*, **1994**, *49*, 22, 3773.
- [3] G. Madras, B.J. McCoy, *Chemical Engineering Science*, **1997**, *52*, 16, 2707.
- [4] J.R. Wünsch, *Polystyrene: Synthesis, Production and Applications*, Rapra Technology Ltd., Shropshire, UK, **2000**.
- [5] A.W. Hui, A.E. Hamielec, *Journal of Applied Polymer Science*, **1972**, *16*, 749.
- [6] E. Vivaldo-Lima, A. Hamielec, P.E. Wood, *Polymer Reaction Engineering*, **1994**, 2, 1-2, 17.
- [7] C. Kotoulas, A. Krallis, P. Pladis, C. Kiparissides, *Macromolecular Chemistry and Physics*, **2003**, *204*, 1305.
- [8] G.V. Korolev, M.P. Berezin, V.P. Grachev, I.N. Zyuzin, *Polymer Science Series A*, **2006**, *49*, 3, 421.
- R.A. Hutchinson, A. Penlidis, *Free-Radical Polymerization: Homogeneous* Systems, in *Polymer Reaction Engineering*, Blackwell Publishing, Oxford, 2007, ch. 3, p. 118.
- [10] J. Gao, A. Penlidis, *Reviews in Macromolecular Chemistry and Physics*, **1996**, *C36*, 2, 199.
- [11] J. Gao, K.D. Hungenberg, A. Penlidis, *Macromolecular Symposia*, **2004**, *206*, 509.
- [12] M.J. Scorah, R. Dhib, A. Penlidis, *Chemical Engineering Science*, **2006**, *61*, 4827.
- [13] R.A.F. Machado, J.C. Pinto, P.H.H. Araújo, A. Bolzan, *Brazilian Journal of Chemical Engineering*, **2000**, *17*, 4, 395.
- [14] G. Kalfas, W.H. Ray, *Industrial and Engineering Chemistry Research*, **1993**, *32*, 1822.
- [15] A.-P. Chemicals, *Product Data Sheet.* 2009.

- [16] K.W. Wu, H.Y. Hou, C.M. Shu, *Journal of Thermal Analysis and Calorimetry*, **2006**, *83*, 1, 41.
- [17] M.S. Kharasch, A. Fono, W. Nudenberg, *Journal of Organic Chemistry*, **1951**, *16*, 1, 105.
- [18] M. Zhang, W.H. Ray, *Journal of Applied Polymer Science*, **2001**, *86*, 1630.
- [19] M.A. Villalobos, A.E. Hamielec, P.E. Wood, *Journal of Applied Polymer Science*, **1993**, *50*, 327.
- [20] D.N. Butala, W.R. Liang, K.Y. Choi, *Journal of Applied Polymer Science*, **1992**, 44, 1759.
- [21] K.D. Hungenberg, Personal Communication, 2010, Kingston.
- [22] Y.-C. Kim, B.J. McCoy, *Industrial and Engineering Chemistry Research*, **2000**, *39*, 2811.
- [23] F. Xue, D. Takeda, T. Kimura, M. Minabe, *Polymer Degradation and Stability*, **2004**, *83*, 461.
- [24] F.R. Mayo, Journal of the American Chemical Society, 1968, 90, 5, 1289.
- [25] J.H. Coco, W.A. Pryor, *Macromolecules*, **1970**, *3*, 5, 500.
- [26] D. Greszta, K. Matyjaszewski, *Macromolecules*, **1996**, *29*, 7661.
- [27] Y. Fu, M.F. Cunningham, R.A. Hutchinson, *Macromolecular Reaction Engineering*, **2007**, *1*, 243.
- [28] W.A. Pryor, L.D. Lasswell, Advances in Free-Radical Chemistry, 1975, 5, 27.
- [29] K.S. Khuong, W.H. Jones, W.A. Pryor, K.N. Houk, *Journal of the American Chemical Society*, **2005**, *127*, 1265.
- [30] J.D. Campbell, F. Teymour, M. Morbidelli, *Macromolecules*, 2003, 36, 15, 5491.
- [31] J.D. Campbell, F. Teymour, M. Morbidelli, *Macromolecules*, 2003, 36, 15, 5502.
- [32] J.G. Braks, R.Y.M. Huang, Journal of Applied Polymer Science, 1978, 22, 3111.
- [33] D. Mikulášová, V. Chrástová, P. Citovický, *European Polymer Journal*, **1973**, *10*, 551.
- [34] B. Boutevin, D. Bertin, *European Polymer Journal*, **1999**, *35*, 815.

- [35] S. Santanakrishnan, L. Tang, R.A. Hutchinson, M. Stach, I. Lacík, J. Schrooten, P. Hesse, M. Buback, *Macromolecular Reaction Engineering*, **2010**, *4*, 499.
- [36] E. Saldivar-Guerra, J. Bonilla, G. Zacahua, M. Abores-Velasco, *Journal of Polymer Science: Part A: Polymer Chemistry*, **2006**, *44*, 6962.
- [37] D.A. Canelas, D.E. Betts, J.M. DeSimone, *Macromolecules*, 1995, 29, 2818.
- [38] A.E. Hamielec, J.W. Hodgins, K. Tebbens, *American Institute of Chemical Engineers Journal*, **1967**, *13*, 6, 1087.
- [39] A.V. Tobolsky, J. Offenbach, *Journal of Polymer Science*, **1955**, *16*, 311.
- [40] J.P. Van Hook, A.V. Tobolsky, *Journal of Polymer Science*, **1958**, *33*, 429.
- [41] M.S. Matheson, E.E. Auer, E.B. Bevilacqua, E.J. Hart, *Journal of the American Chemical Society*, **1951**, *73*, 1700.
- [42] F.L. Marten, A.E. Hamielec, *Journal of Applied Polymer Science*, **1982**, 27, 489.
- [43] W.Y. Chiu, W. Charratt, D.S. Soong, *Macromolecules*, **1983**, *16*, 348.
- [44] E.-H. Wolff, A.N. René Bos, *Industrial and Engineering Chemistry Research*, **1997**, *36*, 1163.
- [45] P. Rivero, *Journal of Polymer Research*, **2004**, *11*, 309.
- [46] C.M. Vrentas, J.L. Duda, *Journal of Polymer Science Part B Polymer Physics*, **1984**, 22, 3, 459.
- [47] D.S. Achilias, C. Kiparissides, *Macromolecules*, **1992**, *25*, 3739.
- [48] M.A. Dubé, J.B.P. Soares, A. Penlidis, A.E. Hamielec, *Industrial and Engineering Chemistry Research*, 1997, 36, 966.
- [49] G.T. Russel, D.H. Napper, R.G. Gilbert, *Macromolecules*, **1988**, *21*, 2133.
- [50] H.K. Mahabadi, K.F. O'Driscoll, *Macromolecules*, **1977**, *10*, 1, 55.
- [51] F. Briers, D.L. Chapman, E. Walters, *Journal of the Chemical Society*, **1926**, 562.
- [52] T. Fukuda, Y.-D. May, H. Inagaki, *Macromolecules*, **1985**, *18*, 17.
- [53] G.G. Odian, *Priniciple of Polymerization*, John Wiley & Sons, Inc., Hoboken, USA, **2004**.

- [54] M. Buback, F.-D. Kuchta, *Macromolecular Chemistry and Physics*, **1995**, *196*, 1887.
- [55] M. Buback, F.-D. Kuchta, *Macromolecular Chemistry and Physics*, **1997**, *198*, 1455.
- [56] M. Buback, C. Kowollik, C. Kurz, A. Wahl, *Macromolecular Chemistry and Physics*, **2000**, *201*, 464.
- [57] S. Beuermann, M. Buback, *Progress in Polymer Science*, 2002, 27, 191.
- [58] Y. Fu, A. Mirzaei, M.F. Cunningham, R.A. Hutchinson, *Macromolecular Reaction Engineering*, **2007**, *1*, 425.
- [59] A. Keramopoulos, C. Kiparissides, *Macromolecules*, **2002**, *35*, 4155.
- [60] R. Dhib, J. Gao, A. Penlidis, *Polymer Reaction Engineering*, **2000**, *8*, 4, 299.
- [61] J. Belincanta-Ximenes, P.V.R. Mesa, L.M.F. Lona, E. Vivaldo-Lima, N.T. McManus, A. Penlidis, *Macromolecular Theory and Simulation*, **2007**, *16*, 194.
- [62] S. Wu, T.J. Harris, K.B. McAuley, *The Canadian Journal of Chemical Engineering*, **2011**, *89*, 148.
- [63] S. Wu, K.B. McAuley, T.J. Harris, *Canadian Journal of Chemical Engineering*, **2009**, *89*, 1, 148.
- [64] D.E. Thompson, K.B. McAuley, P.J. McLellan, *Macromolecular Reaction Engineering*, **2009**, *3*, 130.
- [65] K.Z. Yao, B.M. Shaw, B. Kou, K.B. McAuley, D.W. Bacon, *Polymer Reaction Engineering*, **2003**, *11*, 3, 563.
- [66] K.A.P. McLean, K.B. McAuley, *Canadian Journal of Chemical Engineering*, *Accepted* **2011**.
- [67] M. Wulkow, *Macromolecular Reaction Engineering*, **2008**, *2*, 6, 461.
- [68] M. Schwaab, J.C. Pinto, *Chemical Engineering Science*, **2007**, *62*, 2750.
- [69] M. Schwaab, L.P. Lemos, J.C. Pinto, *Chemical Engineering Science*, **2008**, *63*, 2895.
- [70] L. Cavin, A. Rouge, T. Meyer, A. Renken, *Polymer*, 2000, 41, 3925.
- [71] W.J. Yoon, K.Y. Choi, *Polymer*, **1992**, *33*, 21, 4582.

[72] T. Kothe, H. Fischer, *Journal of Polymer Science: Part A: Polymer Chemistry*, **2001**, *39*, 4009.

Chapter 4 – Conclusions and Recommendations

4.1 Conclusions

A mathematical model is implemented to describe the bulk thermally-initiated freeradical polymerization of styrene between 100 and 170 °C in Predici[™]. Implementation of a chain-transfer-to-adduct reaction required explicit tracking of the styrene adduct concentration, which in turn required use of a full two-step thermal initiation reaction mechanism. The autoacceleration model first developed by Marten and Hamielec and extended by several researchers^[1-5] was used to account for viscosity effects on kinetic coefficients. An attempt was made to rank all 40 adjustable model parameters according to the size of their influence on predictions, uncertainty in initial values, and correlation among their effects,^[6, 7] using experimental settings used to obtained predictions of literature conversion and molecular weight distribution data.^[8-10] It was possible to rank the top 34 most-estimable parameters before numerical problems were encountered. Parameter selection tools were used to determine that estimation of the top four parameters should result in the lowest mean-squared error predictions. Estimating the rate coefficient for transfer to adduct (k_{fdo}) , the activation energies for transfer to adduct, primary-radical generation $((E_a/R)_{fd})$ and $(E_a/R)_i$) and adduct decomposition to two monomers $((E_a/R)_{1/-1})$ reduced the value of the objective function from 45300 to 10600. Despite this large improvement in model fit, some mismatch in the onset point for autoacceleration was observed. Two key parameters that govern the onset point for autoacceleration, K_{ref} and E_{cr}, were tuned manually to ensure that diffusion control for the

chain-termination reaction occurred at the correct point along the conversion curves. Subsequent parameter estimation resulted in a slight improvement in the value of the objective function (10200) and in better trends in the conversion curves. Good fits were obtained for conversion vs. time data collected between 100 and 170 °C as well as the single MWD curve (at 100 °C). Simulations were used to confirm that high-temperature chain-end thermal degradation reactions had little effect on the model predictions at or below 170 °C, which is the maximum temperature considered in this study.

The predictive capabilities of the model described in Chapter 2 were assessed by comparing model predictions to previously neglected data from thermally initiated polymerization experiments. In particular, an additional conversion profile was used, as well as number- and weight-average molecular weight data. It was shown that the model could predict new conversion data quite well, but that there was appreciable mismatch between M_n and M_w predictions and the data, especially at low reaction times. This mismatch could be attributed to high instantaneous number and weight average molecular weights in the first seconds of the simulation. These high molecular weights resulted from the low initial adduct and radical concentrations. In light of this additional information, the assumption that the zero initial adduct concentration was deemed unjustifiable. Use of the stationary-state hypothesis to calculate the initial adduct concentration successfully reduced early average molecular weight predictions and improved trends in model predictions. Parameter ranking and estimation were repeated using all available conversion and molecular weight data from thermally-initiated polymerization experiments. Six parameters $(k_{fdo}/k_{po}, (E_a/R)_1, (E_a/R)_i, (E_a/R)_{1/-1}, [(E_a/R)_{fd}-(E_a/R)_p]$ and k_{10}) were selected for estimation which reduced the objective function by 97 %. With the

inclusion of additional data, more parameters could be estimated compared to the parameter estimation performed Chapter 2, which resulted in only four selected parameters.^[11]

Several attempts were then made to fit additional data obtained from DCP- and BPOinitiated styrene polymerization experiments.^[9, 10] After parameter estimation, trends in the M_n and M_w predictions did not match the data well. To improve initial model predictions, parameters that govern transfer-to-adduct (k_{fdo}/k_{po}), chemical initiation (k_{dDCPo} , (E_a/R)_{dDCP} and k_{dBPOo}) and autoacceleration (A, K_{ref}) were tuned by hand. Additionally, kinetic coefficients for peroxide-induced mid-chain scission reactions (k_{sDCPo} , k_{sBPOo}) were set to 0 mol L^{-1} s⁻¹ to reduce the noticeable reduction in molecular weight predicted at high conversions which was not observed in the literature data. Note, however, that mid-chain scission might occur in situations where monomer concentrations are low and peroxide radical concentrations are high. In addition, chain transfer to monomer (which has been used by many modelers to help fit experimental molecular weight data^[1, 8, 10, 12-14]) was implemented using the literature kinetic coefficients.^[8]

The parameter ranking algorithm and parameter selection techniques demonstrated in Chapter 2 were used to select nine parameters $(k_{dBPOo}, k_{fdo}/k_{po}, [(E_a/R)_{fd}-(E_a/R)_p], (E_a/R)_i,$ $(E_a/R)_1$, A, k_{dDCPo} , $(E_a/R)_{dDCP}$ and V_{fmj}) for estimation, which resulted in a 73 % improvement in the value of the objective function compared to predictions generated using literature values. Despite this large improvement in the value of the objective function, there was still some mismatch between the literature data and model predictions. The model by Kotoulas et al. was able to more closely match experimental data generated by that lab than the model described in this work. However, Kotoulas at al. did not attempt to for or predict data from other labs. These methods allowed the modeling effort to focus on modifications to the model structure and initial parameter guesses instead of selection and estimation of parameters. More model structures and initial parameter sets were investigated than would have been possible without the use of the automated parameter ranking and selection techniques. In the future, model predictions will be compared to a large set of proprietary industrial styrene polymerization data. Using this more extensive data set, the parameter ranking and estimation algorithm should select more parameters for estimation.

Summarized below are the most important conclusions derived from the results of this styrene polymerization modeling project.

- The statistical techniques employed to rank, select and estimate parameters were useful and allowed for exploration of the model structure and investigation of local minima. Parameter scaling was valuable for including information concerning the initial uncertainty in the literature parameter values, so that well-known parameters were not selected for estimation.
- Although the automated parameter selection and estimation techniques were helpful, considerable use of scientific and engineering judgement was required to obtain good fits and parameter values that resulted in satisfactory trends in conversion and molecular weight predictions. Modelers judge the quality of model predictions by looking at slopes and inflection points, which are not featured in

typical weighted nonlinear least-squares objective functions for parameter estimation.

- After final parameter estimation, an improvement of 73 % was obtained in the weighted nonlinear least squares fit between model predictions and experimental data compared with predictions obtained using initial literature parameter values.
- Because precise initial estimates were available from the literature for some important kinetic parameters and data were available from only 14 experimental runs, estimation of only 9 of the 48 parameters could be justified using Wu's parameter selection criterion.
- Both chain transfer to adduct and chain transfer to monomer may be important for controlling average molecular weights. Unfortunately, there is insufficient information in the available data to justify estimation of kinetic parameters associated with chain transfer to monomer.
- Since chain transfer to adduct is important for accurate predictions of molecular weights, it is important to use a realistic value for the initial adduct concentration when simulating reactor behaviour. Better predictions are obtained when the stationary-state hypothesis is used to calculate the initial concentration of adduct than when an initial concentration of zero is assumed.
- Inclusion of peroxide-induced mid-chain scission was not required to obtain accurate predictions for average molecular weights at high conversions.

4.2 Recommendation for Future Work

- 1. To develop a model for the industrial production of expandable polystyrene, it will be important to incorporate a diluent (blowing agent) such as *n*-pentane into the model structure. Most importantly, the effects of this blowing agent on viscosity should be considered, as viscosity influences autoacceleration behaviour.^[9] After implementation of a diluent species and its influence on autoacceleration, parameter ranking and estimation should be performed once more using additional data collected from experiments involving a blowing agent. An initial value will be required for the free volume parameter associated with the blowing agent. To my knowledge, a literature value for this parameter does not exist for *n*-pentane diluent and so I recommend using an initial value of $V_{fmj} = 0.912$ which is the analogous value for styrene used in the current model.
- 2. To assess the importance and severity of peroxide-induced mid-chain scission under industrial conditions, additional experimental runs should be performed with emphasis placed on long reactions times in the presence of peroxide initiators. Near the end of the reaction, after nearly all monomer is consumed, average molecular weight trend behaviour may be influenced by these degradation reactions. Fitting parameters using this additional data should yield better estimates of k_{sDCPo} and k_{sBPOo}.
- 3. To determine better values for the rate coefficients governing chain transfer to adduct and chain transfer to monomer, specific experimental studies should be

performed. Carefully designed experiments will be required to determine the relative rates of these chain transfer reactions.

4.3 References

- [1] M.J. Scorah, R. Dhib, A. Penlidis, *Chemical Engineering Science*, **2006**, *61*, 4827.
- [2] C.M. Vrentas, J.L. Duda, *Journal of Polymer Science Part B Polymer Physics*, **1984**, 22, 3, 459.
- [3] D.S. Achilias, C. Kiparissides, *Macromolecules*, **1992**, *25*, 3739.
- [4] M.A. Dubé, J.B.P. Soares, A. Penlidis, A.E. Hamielec, *Industrial and Engineering Chemistry Research*, **1997**, *36*, 966.
- [5] G.T. Russel, D.H. Napper, R.G. Gilbert, *Macromolecules*, **1988**, *21*, 2133.
- [6] K.Z. Yao, B.M. Shaw, B. Kou, K.B. McAuley, D.W. Bacon, *Polymer Reaction Engineering*, **2003**, *11*, 3, 563.
- [7] D.E. Thompson, K.B. McAuley, P.J. McLellan, *Macromolecular Reaction Engineering*, **2009**, *3*, 130.
- [8] A.W. Hui, A.E. Hamielec, *Journal of Applied Polymer Science*, **1972**, *16*, 749.
- [9] M.A. Villalobos, A.E. Hamielec, P.E. Wood, *Journal of Applied Polymer Science*, **1993**, *50*, 327.
- [10] C. Kotoulas, A. Krallis, P. Pladis, C. Kiparissides, *Macromolecular Chemistry and Physics*, **2003**, *204*, 1305.
- [11] J.D. Woloszyn, K.B. McAuley, *Macromolecular Reaction Engineering*, **2011**, *5*, 9-10, 453.
- [12] D. Greszta, K. Matyjaszewski, *Macromolecules*, **1996**, *29*, 7661.
- [13] J. Gao, K.D. Hungenberg, A. Penlidis, *Macromolecular Symposia*, **2004**, *206*, 509.
- [14] J. Belincanta-Ximenes, P.V.R. Mesa, L.M.F. Lona, E. Vivaldo-Lima, N.T. McManus, A. Penlidis, *Macromolecular Theory and Simulation*, **2007**, *16*, 194.
Appendix 1 – Use of Predici

Because of the nature of the algebraic equations used in the model, as well as the requirements of PrediciTM, several tricks were required to produce the desired outputs using PrediciTM.

A.1.1 Numerical Settings and Tolerances

The length and number of time steps PrediciTM uses during a simulation can be modified using what is called the model's 'accuracy' which can be inputted by the user in the model Workshop dialogue window. A lower 'accuracy' value results in smaller time steps within a simulation, producing more accurate simulation results, with longer simulation times, which could be confusing. If the 'accuracy' value is set to a very small number, simulations fail (without any error messages or other clues) presumably because the number of calculations becomes too large. Conversely, 'accuracy' values that are too large can lead to inaccurate model predictions. It is important to select an 'accuracy' value that will lead to sufficiently accurate simulation results and simulation times that are not too long, for the entire range of conditions that will be encountered during the modeling work. Selection of an appropriate 'accuracy' value in this work was achieved by running the simulations with smaller and smaller 'accuracy' values using representative recipes and examining the resulting simulation results and simulation times. 'Accuracy' values were always selected to ensure that no noticeable difference could be observed in plots of concentrations, M_w , M_n and MWD when a smaller accuracy value (i.e., half the size) was used for the simulation.

A.1.2 Calculation of k_i, k_{dcp} and k_{bpo}

Predici'sTM library of reaction mechanisms is quite large and contains many commonly observed reaction types in polymerization systems. Once a user has chosen the mechanisms for his or her model, there are three standard ways to input values for the associated rate coefficients. The simplest method is to input a fixed rate-constant value in the parameter's dialogue window (that will not respond to changes in temperature) and then link that parameter to the appropriate reaction mechanism. A modeler may also use coefficients involving the classical Arrhenius expression (Equation 2.21 in Chapter 2), with a frequency factor, A, and an activation energy divided by the universal gas constant, (E_a/R) . Lastly, a user may opt to write his or her own function dictating the behaviour of the rate coefficient for the reaction, which will run each time Predici™ requires the value of the coefficient (i.e., at every time step of the simulation). This function file method is helpful in cases where a reparameterized Arrhenius expression is desired (see Equation 2.20 in Chapter 2). In nearly all circumstances, one of these three methods of rate coefficient input is sufficient for model building. However, a situation involving the initiation mechanism is described below where a more complicated method of rate coefficient input is required.

Inputting the rate coefficient for free-radical initiation in PrediciTM can be achieved by the first or second method described above. However, the use of a function file for initiation reactions is reserved for calculating the efficiency factor, f, instead of computing the reaction rate coefficient itself. As discussed in the Introduction section in Chapter 2, the efficiency factor accounts for the possibility that a pair of free radicals, produced by thermal decomposition of an initiator molecule, may recombine, or react to form nonpropagating molecules, rather than initiating new polymer chains. To use a reparameterized Arrhenius expression to calculate the rate coefficient dictating the rate of this initiation reaction, a modeller must write a function file that calculates a rate coefficient value and saves this value as an artificial parameter. This artificial parameter can then be included as if it were a fixed rate constant in the parameter's dialogue window, which is linked to the initiation reaction. Note that this "fixed" rate constant value will be updated as reaction conditions change, because of the calculations in the function file. It should be noted that for Predici™ to calculate a value of the initiation rate coefficient at each time step of a simulation, the function file must be included in the model's library of function files, available through the 'Workshop' menu.

A.1.3 Characteristic Backbiting/β-scission Reaction

As described in the Introduction section of Chapter 2, one degradation reaction that can occur at high temperatures is backbiting by the radical chain end at the third, fifth or seventh carbon from the end along the backbone of the polymer chain, followed by β scission. If backbiting occurs at either the third or seventh positions, the polymer will fragment into a living polymer chain that is two or four monomer units shorter, respectively, and a corresponding oligomer. However, if backbiting occurs at the fifth position, the chain can undergo one of two possible scission processes. One outcome yields a living radical chain three units shorter than the original chain and a styrene trimer. The other reaction pathway yields a dead polymer chain and a dimer radical capable of propagation.^[1, 2]

In Predici[™] there is no pre-set reaction to directly describe the second possible reaction pathway for 1:5 backbiting. As shown below, I simulate this second pathway for 1:5 scission using two fictitious reactions in series:

$$P_n \xrightarrow{k_{2b}} P_{n-2} + FakeDimer$$
 (A.1.1)

$$P_{n-2} + FakeDimer \xrightarrow{very fast} D_{n-2} + DimerRadical$$
 (A.1.2)

A very large rate coefficient is used for the second fictitious reaction to ensure that all of the FakeDimer that is generated during the simulation is immediately consumed. The rate coefficient used for the first fictitious step is the value of the rate constant for the real overall reaction, as determined by Campbell.^[1, 2] This overall reaction is:

$$P_n \xrightarrow{k_{2b}} D_{n-2} + DimerRadical$$
 (A.1.3)

Similar tricks could be used, if necessary, for other backbiting reactions that occur during free-radical polymerization.

A.1.4 Autoacceleration

Autoacceleration plays an important role in the bulk polymerization of styrene. Coding of Hui and Hamielec's break-point model proved non-trivial. The equations presented Table 2.3 and again in Table 3.3 were used to govern autoacceleration. In the first phase of autoacceleration, $k_{tc,seg}$ and $k_{td,seg}$ are calculated and used in place of k_{tc} and k_{td} . K_{cr} is calculated at the beginning of the simulation and K is calculated at each time step using its function file in the model's library of function files. These two values are compared at each time step throughout the simulation. Simultaneously, the total free volume in the system is calculated and compared to $V_{f,crm}$ and $V_{f,creff}$ for determination of the onset of the third and fourth phases of autoacceleration, respectively.

In the time step at which K becomes greater than K_{cr} , the available free volume and weight-average molecular weight are both saved to artificial parameters for use in calculating $k_{tc,trans}$ and $k_{td,trans}$. The diffusion-controlled rate coefficients are then used to dictate the rates of termination by combination and disproportionation.

When the total free volume in the system falls below $V_{f,crm}$, $k_{p,eff}$ is linked to the propagation reaction mechanism. The three initiation reaction rate coefficients (k_i , k_{dDCP} and k_{dBPO}) are treated in a similar manner. Three critical free volume values are defined

and compared against the available free volume in the system at each time step of the simulation. Note that the ratio $V_{f,creff}/V_{f,crm}$ is treated as a parameter that can be estimated. As free volume falls below each of these three critical values $f_{i,eff}$, $f_{1,eff}$ or $f_{2,eff}$ is calculated and used in place of f_i , f_1 , or f_2 .

A.1.5 Excel Automation

As discussed in Chapter 2, the first step of an estimability analysis is to generate the sensitivity matrix, Z. In the current research the partial derivatives in Z were generated difference approximations. First, simulations were conducted using initial values for all parameters and then the same predictions were generated with each parameter value increased by 5 %. To build a Z-matrix using a version of the model containing 40 parameters which was fitted using 520 data points (conversion, M_n, M_w and MWD), all simulations were run 41 times and 20800 sensitivity coefficients were calculated. Without automation, calculating and manipulating the elements of Z would be very time consuming. Predici[™], however, contains an Object Linking and Embedding (OLE) functionality which allows it to be slaved to Microsoft's[™] Excel[™]. Through use of Excel's[™] Visual Basic for Applications[™] (VBA) tools, it is possible to set up series of simulations whose outputs can be saved directly into an Excel[™] spreadsheet.

The VBA code that I developed for interfacing $Excel^{TM}$ with PrediciTM is relatively straightforward, because saving conversion, M_n and M_w predictions from PrediciTM is trivial. However, there is no pre-set way to export MWD predictions from PrediciTM using

the OLE functionality. The recommended method of MWD output into Excel[™] described in the Predici[™] documentation^[3] requires a loop that cycles through an object describing the molecular weight distribution of the dead polymer. At each chain-length value of interest, a function in the VBA code stores the concentration (mol volume⁻¹) of the polymer chains of that length in a matrix. To obtain MWD predictions with typical units used in gel permeation chromatography, the following transformation is used:^[3]

$$\frac{\mathrm{dw}}{\mathrm{d}\log(\mathrm{MW})}\Big|_{i} = \left(\frac{\left([\mathrm{D}]_{i} \cdot 10^{(2\log(i))}\right)}{\mathrm{M}_{1}}\right) \tag{A.1.4}$$

where, $[D]_i$ is the concentration of dead polymer chains of length i (number of monomer units) and M_1 is the 1st moment of the molecular weight distribution of dead polymer chains. These transformed MWD predictions are then exported to ExcelTM for use in computing elements of the Z matrix.

A.1.6 Measured Data Files

Predici[™] uses formatted Measured Data Files (MDFs) to read in experimental data for comparison against model predictions. There are several rules governing the correct format of these files, which are discussed in the Predici[™] documentation.^[3] However, I describe a case here for which the documentation is not straightforward. When performing parameter estimation with Predici[™], it is necessary to include MDFs in the dialogue window of the parameter estimation. Within each of these MDFs is a line dictating what recipe file will be used to govern the conditions at which the model will

run. For example, the recipe file contains the initial concentrations of each of the components in the simulation, as well as the temperature, and pressure if necessary. If desired, an MDF can supersede its associated recipe file and control the initial conditions of the simulation. Note that this functionality can cause difficulties to an unsuspecting user. While implementing our model in Predici[™] I found that if the initial concentration of initiator was not included at the 'zero second' time step of an MDF, the software took this to mean that the concentration was zero rather than the concentration that was specified in the recipe file. To rectify this behaviour the 'zero second' time step for each variable in each MDF was removed. There was no need to use any data collected at time zero for fitting model parameters.

A.1.7 Scaling Factors and the Objective Function

As discussed in Chapter 2, the objective function, J, is a weighted-sum-of-squared errors (SSE) between the model predictions and the data:

$$J = \sum_{i=1}^{r} \sum_{j=1}^{d_i} \sum_{k=1}^{n_{ij}} \frac{\left(y_{m,ijk} - y_{ijk}\right)^2}{s_{yj}^2}$$
(A.1.5)

PrediciTM uses a slightly different default objective function to assess the fit between model predictions and measured data:

$$J = \sum_{i=1}^{r} \sum_{j=1}^{d_i} \sum_{k=1}^{n_{ij}} \frac{\left(y_{m,ijk} - y_{ijk}\right)^2}{\left(w_{yj}\right)^2},$$
(A.1.6)

where,

$$w_{yj} = \max(s_{yj}, y_{ijk}). \tag{A.1.7}$$

In this expression, s_{yj} is a user-inputted value for the scaling of the measurement of type j. However, if no value is inputted by the user, or if the value of s_{yj} is lower than the measurement itself, the actual measured value, $y_{m,ijk}$, is used in its place. Since the parameter selection method developed by Wu et al.^[4, 5] requires calculation of the SSE expression shown in Equation A.1.5, a work around was required to ensure that PrediciTM generated appropriate values for the objective function. As such, artificial s_{yj} values, augmented by a common factor of 1000, are used in Predici'sTM data fitting algorithm so that each s_{yj} value is larger than its corresponding y_{ijk} value. This reduces the magnitude of J by the same factor. Additionally, it should be noted that PrediciTM actually uses a 'relative total residual' to quantify the difference between measured data and model predictions:

$$r_{\rm rel} = \frac{1}{\sqrt{N}} \sqrt{\rm SSE} \tag{A.1.8}$$

where, N is the total number of data values used in model fitting and SSE is the objective function value, J, shown above in Equation A.1.6. In order to use the parameter selection algorithm developed by Wu et al.^[4, 5] a reverse transformation to obtain the SSE values from r_{rel} values (as well as to undo the artificially augmented scaling factors) is applied to the objective function values outputted by PrediciTM.

A.1.8 Convergence Criteria

To define the numerical tolerance used in Predici's[™] parameter estimation algorithm, the term 'accuracy' is used in the parameter estimation dialogue window where a value can be inputted by the user. After each candidate set of parameters is used to generate predictions of the data, the parameter estimation algorithm calculates the objective function value. It then compares the most recent value the objective function, J_n, to its previous value, J_{n-1} . If the difference between these two objective functions $(J_{n-1} - J_n)$ is positive and greater than the value inputted for the estimation's 'accuracy', the algorithm performs another iteration and attempts to find better parameter values. If (J_{n-1} - J_n) is positive and smaller than the 'accuracy' the algorithm will stop and declare that the convergence criteria have been achieved. Lastly, if $(J_{n-1} - J_n)$ is negative, that is, the most recent value of the objective function is worse than its previous value, then the algorithm will attempt a different set of parameter values. For the work described in this thesis, an 'accuracy' value of 0.5 % of the original objective function value was used, which ensured sufficiently accurate parameter estimation results, while keeping the iterations used in each estimation at a reasonable number.

A.1.9 Outputting PrediciTM Results to Excel

Obtaining easily manipulated results from a Predici[™] parameter estimation is relatively simple. After completing an estimation, a user can right-click on coefficient information section of the 'Parameter Estimation - Survey' window and select the 'Excel Output'

option. This will automatically open a blank Excel[™] file and fill it with worksheets corresponding to each of the MDFs used in estimation, with the exception of the MWD data sets. To get comparisons of MWD predictions with measured data files, the user must rerun an estimation using the best parameter values available as initial guesses and manually interrupt the algorithm as it calculates the difference between the MWD predictions and data. The modeller can then right-click on the MWD window (which contains two plots, one for the model predictions and one for the measured data) and select 'Graphs to Excel' which will again open a blank Excel[™] file and write the plot information to it. This technique must be applied for each MWD data set used in model fitting.

A.1.10 Manual Tuning of Parameters

As demonstrated in Chapter 3, it is often necessary to use scientific and engineering judgement to manually tune parameter values to address systematic trends in predictions. The easiest way to tune a particular parameter is to set all of the parameters at the values which give the most recent best fits to the data and then to use Predici's[™] internal parameter estimation routine to estimate the single parameter of interest. It can be helpful only to include those data sets which exhibit disagreement with predictions. If Predici[™] cannot find a better estimate for the parameter of interest, it may be necessary to manually change the parameter value (while remaining within the parameter bounds set previously) to obtain a closer match to the data, and then perform the single-parameter estimation.

A.1.11 Calculation of 95 % Confidence Intervals Using Jacobian Matrix

The 95 % confidence intervals for the final parameter estimates in Chapter 3 (Table 3.11) were calculated by generating a Jacobian matrix, *J*, via difference approximations. This matrix was generated in the same way as the Z-matrix for parameter ranking, except scaling factors were not included in the elements of the Jacobian matrix. Once the Jacobian matrix was generated around the final parameter estimates shown in Table 3.11, the following equation was applied to determine the 95 % confidence intervals for each parameter estimate:

$$CI = t_{\nu,\alpha/2} \{ (J^T J)^{-1} SSE \}^{1/2},$$
(A.1.9)

which results in a *p* x *p* matrix, where *p* is the number of parameters estimated. $t_{v, \alpha/2}$ is the t-value from the student t table for n-*p* degrees of freedom. Note that in this case, the number of degrees of freedom is large, because the number of data points (~1000) was number larger than the number of parameters estimated (9), and therefore $t_{v, \alpha/2}$ was taken to be 1.96. *J* is the Jacobian matrix calculated around the final parameter estimates, and contains 9 columns and ~1000 rows. *SSE* is the overall sum of squared error resulting from these final parameter estimates, equal to 34560. The *p* diagonal elements of the CI matrix correspond to the confidence intervals for each of the *p* parameter estimates.

A.1.10 References

- [1] J.D. Campbell, F. Teymour, M. Morbidelli, *Macromolecules*, **2003**, *36*, 15, 5491.
- [2] J.D. Campbell, F. Teymour, M. Morbidelli, *Macromolecules*, **2003**, *36*, 15, 5502.
- [3] M. Wulkow, *Predici: Simulation Package for Polyreactions*. 2003: Rastede, Germany.
- [4] S. Wu, T.J. Harris, K.B. McAuley, *The Canadian Journal of Chemical Engineering*, **2011**, *89*, 1, 148.
- [5] S. Wu, T.J. Harris, K.B. McAuley, *The Canadian Journal of Chemical Engineering*, **2011**, *89*, 2, 325.

Appendix 2 – Peroxide Mid-Chain Scission Kinetics

A.2.1 Peroxide-induced mid-chain scission kinetics

To my knowledge, rate coefficients for Reaction 5 and 6 in Table 3.1 are not available in the literature. McCoy and co-workers determined kinetic coefficient values for the combined mechanisms shown in Equation 3.4.^[1, 2] Note that these authors used di-tertbutyl peroxide (DTBP) as a source of radicals. We use the following treatment to generate initial guesses for the elementary rate coefficients k_{sDCP} and k_{sBPO} .

Near the end of a polymerization, when monomer is nearly depleted, the main peroxide sink is via Reaction 1 and 5 (or 2 and 6). At this point in the reaction, the combined mechanism investigated by Madras and McCoy is valid and the rate of chain scission is given by

$$R_s = k_s(w)[D(w)][0],$$
 (A.2.1)

where $k_s(w)$ is the rate coefficient for scission in L mol_{scission}⁻¹ s⁻¹ (which is a function of the molecular weight of the chain undergoing scission, w), [D(w)] is the concentration of polymer chains of mass w and [O] is the concentration of peroxide species, O. Madras

and McCoy define $k_s(w)$ as κ_s w which can be generalized to give an average rate of scission of,

$$\mathbf{R}_{s} = \kappa \mathbf{M}_{n}[\mathbf{D}][\mathbf{0}], \tag{A.2.2}$$

where M_n is the number average molecular weight of dead polymer chains, and [D] is the overall concentration of dead polymer chains. To generate an expression for the true rate of chain scission throughout the entire process, we equate Equation A.2.2 to the true rate expression for scission used by PrediciTM,

$$R_{s} = \kappa_{strue}(s-1)[D(s)][0^{*}].$$
(A.2.3)

In this rate expression, κ_{strue} is the rate coefficient for scission in L mol_{units}⁻¹ s⁻¹, s is the number of monomer units in the polymer chain undergoing scission, [D(s)] is the concentration of polymer chains of length s and [O^{*}] is the concentration of peroxide radicals. Again, to give an expression for the average rate of chain scission, (s - 1) can be expressed as $(\frac{M_n}{M_m} - 1)$ to give a number average chain length of dead polymer. If we equate Equation A.2.2 and Equation A.2.3, we can get an expression for κ_{strue} . By running simulations at different temperatures with the scission reactions inactive until completion and determining the values of [O], [O^{*}] and \overline{M}_n and calculating the expected κ_s , we get a rough estimate of κ_{strue} .

$$\kappa_{\text{strue}} = \frac{\kappa_{\text{s}} M_{\text{n}}[0]}{\left[\left(\frac{M_{\text{n}}}{M_{\text{m}}}\right) - 1\right][0^*]}$$
(A.2.4)

Table A.2.1 shows the results of simulations run to very high conversions, wherein almost no monomer remains in the reactor. Values of κ_s were calculated using rate coefficient information from Madras and McCoy^[1] and Kim and Madras^[2]. Values of [DCP], [DCP^{*}] and M_n for four different temperatures are taken from PrediciTM predictions. Also shown are values for κ_{strue} at each temperature calculated using Equation A.2.4.

Table A.2.1. Values of calculated and predicted terms used for calculation of κ_{strue} .

Temp.	Ks	M _n	[D]	[DCP]	[DCP*]	K _{strue}
(°C)	$(L g^{-1} s^{-1})$	(g mol ⁻¹)	(L mol ⁻¹ s ⁻¹)	(L mol ⁻¹ s ⁻¹)	$(L mol^{-1} s^{-1})$	(L mol _{units} ⁻¹ s)
120	8.9950x10 ⁻⁹	1.1823×10^5	9.7920x10 ⁻¹	1.0120x10 ⁻²	1.5655x10 ⁻⁹	6.0612×10^{0}
130	4.1553x10 ⁻⁸	1.0713x10 ⁵	9.8330x10 ⁻¹	8.5125x10 ⁻³	2.4426x10 ⁻⁹	$1.5097 \mathrm{x} 10^{1}$
140	1.7825x10 ⁻⁷	8.7564x10 ⁴	9.8621x10 ⁻¹	5.3792x10 ⁻³	3.2512x10 ⁻⁹	$3.0717 x 10^{1}$
150	7.1379x10 ⁻⁷	7.5461x10 ⁴	9.8505x10 ⁻¹	2.5946x10 ⁻³	2.2294x10 ⁻⁹	8.6639x10 ¹

A plot of $ln(\kappa_{strue})$ vs. 1/T is shown in Figure A.2.1. The slope of the plot gives an estimate for the activation energy divided by the universal gas constant for Reaction 5 (and 6) of 3.6225×10^3 K. The intercept corresponds to a frequency factor of 6.1110×10^{-5} L mol⁻¹ s⁻¹.



Figure A.2.1. $\ln(\kappa_{strue})$ vs. 1/T for PS chain scission via DTBP radical attack.

A.2.2 References

- [1] G. Madras, B.J. McCoy, *Chemical Engineering Science*, **1997**, *52*, 16, 2707.
- [2] Y.-C. Kim, B.J. McCoy, *Industrial and Engineering Chemistry Research*, **2000**, *39*, 2811.

Appendix 3 – Detailed Results from Parameter Estimation Studies using Combined Data from Thermal and Chemical Initiation Studies

A.3.1 Assessing Fit to Additional Thermal Polymerization Data

In Chapter 3 model predictions are compared to conversion, M_n , M_w and MWD data from thermal styrene polymerization experiments that we neglected when fitting parameters in Chapter 2 (see parameter values in Table 2.7 and 2.8 in Chapter 2). The full set of comparisons is shown in Figure A.3.1. As discussed in sections 3.3.1 and 3.3.2 of Chapter 3, there is appreciable, systematic mismatch between model predictions and experimental M_n and M_w data. In the early stages of the polymerization, molecular weight averages are far too high, and quickly drop below the desired range. To alleviate this mismatch which was caused low initial adduct concentration, SSH was applied to the initial concentration of adduct as described in Chapter 3, to account for adduct formation prior to polymerization. Figure A.3.2 shows model predictions of the full set of thermal polymerization data after implementation of SSH on $[AH]_o$. Parameter ranking and estimation was repeated using thermal initiation data alone.





Figure A.3.1. Comparisons between model predictions using the parameter values shown in the third column of Table A.3.1 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation styrene polymerization studies. (a) 100 °C^[1]; (b) 100 °C^[1]; (c) 100 °C^[1]; (d) 120 °C^[1]; (e) 120 °C^[1]; (f) 140 °C^[1]; (g) 140 °C^[1]; (h) 150 °C^[2]; (i) 150 °C^[2]; (j) 160 °C (Δ)^[1], (\Diamond)^[2]; (k) 160 °C^[2]; (l) 165 °C^[1]; (m) 170°C^[2]; (n) 170°C^[2].





Figure A.3.2. Comparisons between model predictions after implementation of SSH on $[AH]_o$ (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation styrene polymerization studies. (a) 100 °C^[1]; (b) 100 °C^[1]; (c) 100 °C^[1]; (d) 120 °C^[1]; (e) 120 °C^[1]; (f) 140 °C^[1]; (g) 140 °C^[1]; (h) 150 °C^[2]; (i) 150 °C^[2]; (j) 160 °C (Δ)^[1], (\Diamond)^[2]; (k) 160 °C^[2]; (l) 165 °C^[1]; (m) 170°C^[2]; (n) 170°C^[2].

A.3.2 Parameter Ranking and Estimation Results for Complete Thermal Polymerization Data Set

Parameters were ranked considering all of the thermal polymerization data discussed in Chapter 2 and 3 using the estimability analysis described in Chapter 2. Table A.3.1 shows the ranked list of parameters as well as their initial values. The top ten ranked parameters also appear in Table 3.8. Wu's method indicates that six parameters should be estimated. The resulting estimates for these parameters are shown in the last column of Table A.3.1. The parameter fitting resulted in a large decrease in the value of the objective function, which fell from 565310 to 15490, calculated using Equation 2.22. Comparisons between model predictions and experimental data after parameter fitting are shown below in Figure A.3.3.

Parameter	Initial Value	Estimated Value
k _{fdo} /k _{po}	5.7662x10 ⁻¹	6.7135x10 ⁻¹
$(E_a/R)_1$	$1.1245 \mathrm{x} 10^4$	1.3672×10^4
$(E_a/R)_i$	$1.1974 \mathrm{x} 10^4$	$1.1189 \mathrm{x} 10^4$
$(E_a/R)_{1/-1}$	6.4889x10 ³	6.4561x10 ³
$[(E_a/R)_{fd}-(E_a/R)_p]$	6.3230×10^2	4.5781×10^2
k ₁₀	2.2678x10 ⁻⁹	3.1863x10 ⁻¹⁰
E _{cr}	5.0000×10^3	
А	3.4800x10 ⁻¹	
k _{io}	8.4641x10 ⁻⁵	
α _m	1.0000x10 ⁻³	
k _{po}	3.4387×10^2	
K _{ref}	5.0000×10^2	
δ_{c}	$1.0000 \text{x} 10^{-3}$	
$(E_a/R)_p$	3.9100x10 ³	
k_{tco}/k_{po}	3.2159x10 ⁵	
V _{fcrmo}	3.0621x10 ⁻²	
V_{fmj}	9.1200x10 ⁻¹	
f_{io}	7.0000x10 ⁻¹	
V_{fpj}	8.3500x10 ⁻¹	
$[(E_a/R)_{tc} - (E_a/R)_p]$	-3.1570×10^3	
$\alpha_{\rm p}$	4.8000x10 ⁻⁴	
A _{1/-1}	$6.4000 ext{x} 10^4$	
E _{crm}	1.6700×10^3	
В	1.0000	
	1 7500	
	Parameter k_{fdo}/k_{po} $(E_a/R)_1$ $(E_a/R)_{1/-1}$ $(E_a/R)_{fd}-(E_a/R)_p$ K_{1o} E_{cr} A E_{cr} A K_{io} $C_a/R)_{fd}-(E_a/R)_p$ k_{1o} F_{cr} A K_{ref} δ_c $(E_a/R)_p$ k_{tco}/k_{po} V_{frmj} f_{io} V_{fpj} $(E_a/R)_{tc}- (E_a/R)_p]$ α_p $A_{1/-1}$ E_{crm} B	ParameterInitial Value k_{fdo}/k_{po} $5.7662x10^{-1}$ $(E_a/R)_1$ $1.1245x10^4$ $(E_a/R)_1$ $1.1974x10^4$ $(E_a/R)_{1/-1}$ $6.4889x10^3$ $[(E_a/R)_{fd}-(E_a/R)_p]$ $6.3230x10^2$ k_{1o} $2.2678x10^{-9}$ E_{cr} $5.0000x10^3$ A $3.4800x10^{-1}$ k_{io} $8.4641x10^{-5}$ α_m $1.0000x10^{-3}$ k_{po} $3.4387x10^2$ K_{ref} $5.0000x10^2$ δ_c $1.0000x10^{-3}$ $(E_a/R)_p$ $3.9100x10^3$ k_{tco}/k_{po} $3.2159x10^5$ V_{frinj} $9.1200x10^{-1}$ f_{io} $7.0000x10^{-1}$ V_{fpj} $8.3500x10^{-1}$ V_{fpj} $8.3500x10^{-1}$ E_{crm} $1.6700x10^3$ B 1.0000

Table A.3.1. Ranked list of parameters using estimated values from Chapter 2 as initial guesses





Figure A.3.3. Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.3.1 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation styrene polymerization studies. (a) 100 °C^[1]; (b) 100 °C^[1]; (c) 100 °C^[1]; (d) 120 °C^[1]; (e) 120 °C^[1]; (f) 140 °C^[1]; (g) 140 °C^[1]; (h) 150 °C^[2]; (i) 150 °C^[2]; (j) 160 °C (Δ)^[1], (\Diamond)^[2]; (k) 160 °C^[2]; (l) 165 °C^[1]; (m) 170°C^[2]; (n) 170°C^[2].

A.3.3 Predictions of Thermal and Chemical Data using Parameters Estimated using Thermally Initiated Polymerization Data Only

Figure A.3.4 shows comparisons against literature data obtained using DCP and BPO initiators, estimated parameter values from Table A.3.1 and literature values for the remaining parameters (see the third column of Table A.3.2 for the full list of parameter values).





Figure A.3.4. Comparisons between model predictions using the parameter values shown in the last column of Table A.3.1 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in chemical initiated styrene polymerization studies. (a) 120 °C, (DCP, 4000 ppm)^[2]; (b) 120 °C, (DCP, 4000 ppm)^[2], (c) 130 °C, (DCP, 4000 ppm)^[2]; (d) 130 °C, (DCP, 4000 ppm)^[2]; (e) 130 °C, (DCP, 4000 ppm)^[2]; (f) 140 °C, (DCP, 4000 ppm)^[2]; (g) 140 °C, (DCP, 4000 ppm)^[2]; (h) 140 °C, (DCP, 4000 ppm)^[2]; (i) 150 °C, (DCP, 4000 ppm)^[2]; (j) 150 °C, (DCP, 4000 ppm)^[2]; (k) 90 °C, (BPO, 3050 ppm)^[3]; (l) 90 °C, (BPO, 3050 ppm)^[3].

There is appreciable mismatch in prediction of data obtained from chemically initiated experiments. Final conversions are adequate (Figure A.3.4(a), (c), (f), (j), (k)), but the early rates of polymerization and the initial molecular weight averages are too high

(Figure A.3.4(b), (d), (g), (j), (l)). The overall objective function value associated with this prediction, considering all thermally and chemically initiated polymerization data sets, is 160400. Parameter ranking and estimation was then performed using the full set of thermal and chemical polymerization data.

A.3.4 Parameter Estimation Attempts Using Full Literature Data Set

Determining parameter values capable of predicting both thermally and chemically initiated styrene polymerization data was found to be a non-trivial task. Several parameter ranking and estimation steps were performed before the best predictions were achieved. They are detailed in this section.

A.3.5 Parameter Ranking and Estimation Results: Attempt 1 using Complete Literature Data Set

The results of the parameter ranking algorithm are shown in Table A.3.2 along with initial guesses for each parameter. Wu's parameter selection method indicated that five parameters should be estimated, also shown in Table A.3.2. Comparisons between model predictions and experimental data using these five updated parameter values are shown in Figure A.3.5. The parameter estimation resulted in a large improvement in the value of the objective function, which decreased from 160400 to 46819. There are, however, still some problems with the general trends, especially for chemically initiated polymerization predictions. Molecular weight averages are still much too high in the early stages of

polymerization, although final molecular weights are mostly good. Final conversions are adequate, however, autoacceleration appears to be triggering too late for predictions of the DCP-initiated experimental data, and too early for the BPO experiments. To reduce some of the systemic mismatch in model predictions, hand tuning of key parameters was performed.

Rank	Parameter	Initial Value	Final Value
1	k _{dDCPo}	1.5320×10^{-4}	5.1493×10^{-5}
2	k_{fdo}/k_{po}	6.71351x10 ⁻¹	1.0653
3	$(E_a/R)_{dDCP}$	1.8362×10^4	1.5333×10^4
4	$(E_a/R)_1$	1.3672×10^4	1.3125×10^4
5	$(E_a/R)_i$	1.1189x10 ⁴	1.0332×10^4
6	k ₁₀	3.1863x10 ⁻¹⁰	
7	V_{fmj}	9.1200x10 ⁻¹	
8	k _{dBPO}	1.7508x10 ⁻⁴	
9	α_{m}	1.0000×10^{-3}	
10	E _{cr}	5.0000×10^3	
11	А	3.4800x10 ⁻¹	
12	$(E_a/R)_p$	3.9100x10 ³	
13	k _{io}	8.4641x10 ⁻⁵	
14	K _{ref}	5.0000×10^2	
15	k _{po}	$3.4387 \text{x} 10^2$	
16	V_{fpj}	8.3500x10 ⁻¹	
17	k_{tco}/k_{po}	3.2159×10^5	
18	$[(E_a/R)_{fd}-(E_a/R)_p]$	4.5781×10^2	
19	V _{fcrmo}	3.0621x10 ⁻²	
20	$(E_a/R)_{1/-1}$	6.4561x10 ³	
21	$[(E_a/R)_{td}-(E_a/R)_p]$	-3.1570×10^3	
22	α_{p}	4.8000x10 ⁻⁴	
23	f_{DCP}	7.0000x10 ⁻¹	
24	f_{io}	7.0000x10 ⁻¹	
25	k _{sbpoo}	6.9861x10 ¹	
26	n	1.75	
27	k _{sdcpo}	6.9861x10 ¹	
28	δ _c	1.0000×10^{-3}	
29	В	1.0	
30	E _{crm}	1.6700×10^3	
31	f _{BPO}	7.0000x10 ⁻¹	
32	A _{1/-1}	6.4000x10 ⁴	
33	$(E_a/R)_{sBPO}$	3.6225x10 ³	
34	$(E_a/R)_{sDCP}$	3.6225×10^3	
35	$(E_a/R)_{dBPO}$	1.7000×10^4	

Table A.3.2. Ranked list of parameters using estimated values from fitting of thermally initiated experimental data and results of parameter estimation Attempt 1.









Figure A.3.5. Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.3.2 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].
A.3.6 Hand-Tuning of Parameters k_{fdo}/k_{po} , k_{dDCPo} , $(E_a/R)_{dDCP}$, k_{dBPOo} , and K_{ref} to Improve Trends in Predictions

Implementing SSH on the initial adduct concentration such that some adduct is present at the beginning of each polymerization effectively reduced initial molecular weight averages (see Figure A.3.1 and Figure A.3.2). Hand-tuning of parameters which appear in Equation 3.26, and strongly influence the initial concentration of adduct was performed to try to rectify the initial molecular weights which are still too high (Figure A.3.5(p), (r), (u), (x), (z)). Starting from model predictions shown in Figure A.3.3 and Figure A.3.4 (which correspond to the parameter values shown in the third column of Table A.3.2), several parameters were manually tuned, with varying degrees of success. Finally, the ratio k_{fdo}/k_{po} was chosen for hand tuning, as increasing its value adequately reduced the initial molecular weights for the chemically initiated model predictions, while doing the least harm to predictions of the thermal polymerization data. The value of k_{fdo}/k_{po} was increased from 0.67135 to 1.5, which lies within the uncertainty bounds.

In addition, it is clear that the initial rates of initiation in Figure A.3.3 (o), (q), (t) and (y) for DCP and BPO initiated polymerizations were too high, and so some mild hand tuning of k_{dDCPo} , $(E_a/R)_{dDCP}$ and k_{dBPOo} was done $(k_{dDCPo}$ moved from 1.5320x10⁻⁴ to 1.1131x10⁻⁴ L mol⁻¹ s⁻¹; $(E_a/R)_{dDCP}$ moved from 1.8362x10⁴ to 1.7378x10⁴ K; and k_{dBPOo} moved from 1.7508x10⁻⁴ to 3.1x10⁻⁵ L mol⁻¹ s⁻¹). Finally, K_{ref} was manually tuned from 5.0x10² to 2.75x10² kg^{0.5} mol^{-0.5} to ensure that diffusion control for the termination reactions occurred at the correct point in the polymerization. Figure A.3.6 shows model predictions

obtained using these updated parameter values (without further estimation) which are repeated in Table A.3.3 along with the remaining parameter values. The objective function value for these model predictions is 144350. Using these parameter values as initial guesses, parameter ranking and estimation was again performed.









Figure A.3.6. Comparisons between model predictions using the hand-tuned parameter values shown in the third column of Table A.3.3 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].

A.3.7 Parameter Ranking and Estimation Results: Attempt 2 using Complete Literature Data Set

The ranked parameter list generated with the hand-tuned parameter values discussed above is shown in Table A.3.3 along with their initial values. After parameter estimation, Wu's method indicated that eight parameters should be estimated, which resulted in a decrease in the objective function value from 144350 to 44783. Comparisons between model predictions using these estimated parameters and experimental data are shown in Figure A.3.7. Again predictions of thermal polymerization data are quite good, however, molecular weight averages for chemically initiated model predictions returned to their high initial values. Note that the parameter estimator partially reversed the previous hand tuning on k_{fdo}/k_{po} (see Table A.3.3) in an attempt to fit the initial molecular weights in the thermal polymerization data. The objective function value of 44783 is similar to the result of the previous parameter estimation (Attempt 1) which resulted in an objective function value of 46819, indicating that both sets of parameters give result of a similar quality. Both sets of parameters may represent local minima in the response surface for this system.

Attempt 2.						
Rank	Parameter	Initial Value	Final Value			
1	k_{fdo}/k_{po}	1.5	9.8508x10 ⁻¹			
2	$(E_a/R)_{dDCP}$	1.7378×10^4	1.5865x10 ⁴			
3	$(E_a/R)_1$	1.3672×10^4	1.3154x10 ⁴			
4	$(E_a/R)_i$	1.1189x10 ⁴	1.0515x10 ⁴			
5	Α	3.4800x10 ⁻¹	3.7423x10 ⁻¹			
6	α _m	1.0000x10 ⁻³	1.5000x10 ⁻³			
7	k _{dBPOo}	3.1x10 ⁻⁵	9.2592x10 ⁻⁵			
8	k _{dDCPo}	1.1131x10 ⁻⁴	5.4018x10 ⁻⁵			
9	k ₁₀	3.1863x10 ⁻¹⁰				
10	$(E_a/R)_p$	3.9100x10 ³				
11	k _{io}	8.4641x10 ⁻⁵				
12	E _{cr}	5.0000x10 ³				
13	V _{fmj}	9.1200x10 ⁻¹				
14	α _p	4.8000x10 ⁻⁴				
15	k _{fdo} /k _{po}	4.5781x10 ²				
16	$(E_a/R)_{1/-1}$	6.4561x10 ³				
17	V _{fermo}	3.0621x10 ⁻²				
18	K _{ref}	2.7500×10^2				
19	k _{po}	3.4387x10 ²				
20	$[(E_a/R)_{td}-(E_a/R)_p]$	-3.1570×10^3				
21	k _{tco} /k _{po}	3.2159x10 ⁵				
22	f _{io}	7.0000x10 ⁻¹				
23	δ_{c}	1.0000x10 ⁻³				
24	f ₁₀	7.0000x10 ⁻¹				
25	V_{fpj}	8.3500x10 ⁻¹				
26	n	1.75				
27	E _{crm}	$1.6700 \mathrm{x} 10^3$				
28	A _{1/-1}	$6.4000 \mathrm{x10}^4$				
29	В	1.0				
30	f ₂₀	7.0000x10 ⁻¹				
31	k _{sBPOo}	6.9861x10 ¹				
32	k _{sDCPo}	6.9861x10 ¹				
33	$(E_a/R)_{sBPO}$	3.6225×10^3				
34	$(E_a/R)_{sDCP}$	3.6225x10 ³				

Table A.3.3. Ranked list of parameters after hand tuning transfer-to-adduct, initiatordecomposition and autoacceleration onset parameters and results of parameter estimation Attempt 2.









Figure A.3.7. Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.3.3 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].

A.3.8 Hand-Tuning of Parameters A and K_{ref} to Improve Trends in Predictions

In an attempt to escape the apparent local minimum resulting from parameter estimation Attempts 1 and 2, further hand tuning was done starting from model predictions shown in Figure A.3.6 (with parameters from the third column of Table A.3.3). While initial molecular weight averages for chemically initiated predictions are quite good (Figure A.3.6(p), (r), (u), (x) and (z)), the increases in M_n and M_w at the onset of autoacceleration are not strong enough. One parameter in particular, A (which appears in Equation 3.6 and 3.10) governs the strength of the effect of diffusion control on the termination rate coefficients. Starting with the hand-tuned valuea of k_{fdo}/k_{po}, k_{dDCPo}, (E_a/R)_{dDCP}, k_{dBPOo}, and K_{ref} (which appear with all other parameter values shown in the third column of Table A.3.3) the parameter A was tuned upwards from 3.48×10^{-1} to 5.0×10^{-1} . Since this parameter also appears in one of the equations governing the autoacceleration onset point (Equation 3.10), another parameter responsible for the onset of autoacceleration was modified as well: K_{ref} was tuned from 2.75x10² to 9.50x10² kg^{0.5} mol^{-0.5}. Figure A.3.8 shows initial model predictions compared to experimental data. Note that the increases in M_n and M_w predictions during autoacceleration for DCP and BPO initiated polymerizations now increase in line with the experimental data (Figure A.3.8(p), (r), (u), (x) and (z)). The objective function value associated with the comparisons in Figure A.3.8 is 133375. Another parameter ranking and estimation was performed using these initial parameter values.









Figure A.3.8. Comparisons between model predictions using the hand-tuned parameter values shown in the third column of Table A.3.4 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].

A.3.9 Parameter Ranking and Estimation Results: Attempt 3 using Complete Literature Data Set

Table A.3.4 shows the ranked list of parameters after hand tuning parameters A and K_{ref} as well as the full set of initial values used in parameter estimation. Wu's method indicated that five parameters should be estimated, which results in a reduction in the objective from 133375 to 47764, very similar to the final objective function values resulting from Attempts 1 and 2. The model predictions are very similar to those resulting from parameter estimation Attempt 2 and are therefore not shown here.

Rank	Parameter	Initial Value	Final Value
1	k.	1 1311x10 ⁻⁴	5.0030×10^{-5}
2	L _{dcpo}	1.1511X10	9.9208×10 ⁻¹
2	(E/D)ldopEaD	1.3	1.6922×10^4
3	(E_a/R) kucpeak	1.7378×10^4	1.0823×10^4
4	(E_a/R) KIEaR	1.30/2x10	1.3329X10
5	(E_a/R) KIEaR	1.1189x10 ⁻¹⁰	1.0820x10 ⁺
6	k ₁₀	3.1863x10 ¹⁰	
7	V _{fmj}	9.120x10	
8	k _{dBPOo}	3.1x10 ⁻³	
9	α _m	1.0000x10 ⁻³	
10	E _{cr}	5.0000x10 ³	
11	Α	5.0x10 ⁻¹	
12	$(E_a/R)_p$	3.9100x10 ³	
13	k _{io}	8.4640x10 ⁻⁵	
14	K _{ref}	9.5×10^2	
15	\mathbf{k}_{po}	3.4387×10^2	
16	V _{fpj}	8.3500x10 ⁻¹	
17	k _{tco} /k _{po}	3.2159x10 ⁵	
18	$[(E_a/R)_{fd}-(E_a/R)_p]$	4.5781x10 ²	
19	V _{fcrmo}	3.0621x10 ⁻²	
20	$(E_a/R)_{1/-1}$	6.4561x10 ³	
21	$[(E_a/R)_{tc}-(E_a/R)_p]$	-3.1570×10^3	
22	α _p	4.8000x10 ⁻⁴	
23	f ₁₀	7.0000x10 ⁻¹	
24	f _{io}	7.0000x10 ⁻¹	
25	k _{sBPOo}	6.9861x10 ¹	
26	n	1.75	
27	k _{sDCPo}	6.9861x10 ¹	
28	δ_{c}	1.0000x10 ⁻³	
29	В	1.0	
30	Ecrm	1.6700x10 ³	
31	f ₂₀	7.0000×10^{-1}	
32	A1/-1	$6.4000 ext{x} 10^4$	
33	$(E_a/R)_{eBPO}$	3.6225x10 ³	
34	$(E_a/R)_{sDCP}$	3.6225x10 ³	
35	$(E_a/R)_{dBPO}$	1.7000×10^4	

Table A.3.4. Ranked list of parameters after hand tuning autoacceleration strength parameters and results of parameter estimation Attempt 3.

A.3.10 Hand-Tuning of Parameters k_{sDCPo} and k_{sBPOo} to Improve Trends in Predictions

It is evident that final molecular weight averages predicted for chemically initiated polymerizations are too low, even if autoacceleration triggers strongly enough. This drop in M_n and M_w at high conversions may be induced by mid-chain scission reactions that were included in the model (see Reaction 5 and 6 in Table 3.1). Measured M_n and M_w trends for these experimental conditions show very little or no decrease near the end of the polymerizations (see (\Box) and (\Diamond) symbols in Figure A.3.8(p), (r), (u), (x) and (z)). Starting with the hand-tuned parameter values of k_{fdo}/k_{po}, k_{dDCPo}, (E_a/R)_{dDCP}, k_{dBPOo}, A and K_{ref} (and all other parameters at the value shown in the third column of Table A.3.2) the two rate coefficients governing the rate of mid-chain scission, k_{sDCPo} and k_{sBPOo}, were set to zero in an attempt to ensure that final M_n and M_w values remained at the desired levels after they increased during autoacceleration. Figure A.3.9 shows comparisons of predictions to experimental data after reducing mid-chain scission rate coefficients to zero. The parameter values used to generate the comparisons in Figure A.3.9 are shown in the third column of Table A.3.5. The value of the objective function corresponding to these comparisons is 115900 which is lower than before hand tuning of k_{sDCPo} and k_{sBPOo} .









Figure A.3.9. Comparisons between model predictions using the hand tuned parameter values shown in the third column of Table A.3.5 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].

A.3.11 Parameter Ranking and Estimation Results: Attempt 4 using Complete Literature Data Set

Table A.3.5 shows the ranked list of parameters after hand tuning of the mid-chain scission rate coefficient parameters. According to Wu's method, only two parameters should be estimated and the estimation results in a final objective function value of 38840 (down from 115900) which is the lowest objective function value that was obtained for the entire data set thus far. Note that while previous parameter estimation attempts were unable to achieve good predictions of final molecular weight averages for both thermally and chemically initiated polymerization, the comparisons between model predictions and experimental data shown in Figure A.3.10 show reasonably good predictions of final molecular weight predictions of chemically initiated polymerization data are too high, although the subsequent trends in M_n and M_w are good. Additionally, the estimated value of k_{dBPOo} results in very fast polymerization and poor prediction of autoacceleration as shown in Figure A.3.10(y).

Rank	Parameter	Initial Value	Final Value
1	k _{dBPOo}	3.1x10 ⁻⁵	1.1978x10 ⁻⁴
2	k _{fdo} /k _{po}	1.5	7.3606x10 ⁻¹
3	$(E_a/R)_i$	1.1189x10 ⁴	
4	$(E_a/R)_1$	1.3672x10 ⁴	
5	k _{dDCPo}	1.1131x10 ⁻⁴	
6	Α	5.0000x10 ⁻¹	
7	$[(E_a/R)_{fd}-(E_a/R)_p]$	4.5781x10 ²	
8	$(E_a/R)_{dDCP}$	1.7378x10 ⁴	
9	A _{1/-1}	6.4000x10 ⁴	
10	k ₁₀	3.1863x10 ⁻¹⁰	
11	k _{io}	8.4641x10 ⁻⁵	
12	$(E_a/R)_p$	3.9100x10 ³	
13	$[(E_a/R)_{td}-(E_a/R)_p]$	-3.1570×10^3	
14	E _{cr}	5.0000x10 ³	
15	V_{fpj}	8.3500x10 ⁻¹	
16	k _{tco} /k _{po}	3.2159x10 ⁵	
17	$\alpha_{\rm p}$	4.8000x10 ⁻⁴	
18	f_{io}	7.0000x10 ⁻¹	
19	$(E_a/R)_{1/-1}$	6.4561x10 ³	
20	V _{fmj}	9.1200x10 ⁻¹	
21	V _{fcrmo}	3.0621x10 ⁻²	
22	n	1.75	
23	k _{po}	3.4387x10 ²	
24	f ₁₀	$7.0000 \mathrm{x} 10^{-1}$	
25	α _m	1.0000x10 ⁻³	
26	δ_{c}	1.0000x10 ⁻³	
27	E _{crm}	1.6700×10^3	
28	В	1.0	
29	f_{2o}	7.0000x10 ⁻¹	

Table A.3.5. Ranked list of parameters after hand tuning of mid-chain scission parameters and results of parameter estimation Attempt 4.









Figure A.3.10. Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.3.5 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].

A.3.12 Implementation of Transfer-to-Monomer Reaction Starting with Thermally Tuned Parameters Only

Because some systemic problems were still apparent in predictions of the data and transfer to monomer had not been included in our mechanism, we elected to investigate the potential improvements in fit when both transfer to monomer and transfer to adduct were considered together. It should be noted that Greszta et al. found that implementation of a transfer-to-monomer reaction in their model resulted in negligible change to their molecular weight predictions.^[4] The small rate coefficient and the activation energy used by Greszta et al. (who's model included both transfer to monomer and transfer to adduct) were used as initial parameter guesses (i.e., $k_{fmo} = 2.0856 \times 10^{-1}$ L mol⁻¹ s⁻¹ at 120 °C and (E_a/R)_{fm} = 6.3770 \times 10^3 K).

To investigate the effect of implementing a transfer-to-monomer reaction, initial parameter values from Table A.3.6 were used as initial guesses. Figure A.3.11 shows model predictions with these parameter values. The value of the objective function corresponding to these comparisons is 204310, which is worse than our previous initial objective function values.









Figure A.3.11. Comparisons between model predictions using the hand-tuned parameter values shown in the third column of Table A.3.6 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].

A.3.13 Parameter Ranking and Estimation Results: Attempt 5 using Complete Literature Data Set

Table A.3.6 shows the ranked list of parameters with their initial values used in parameter estimation. The last column of Table A.3.6 also shows the resulting parameter estimates for the nine parameters selected by Wu's method. The value of the objective function fell from 204310 to 116150 which is a very large value for the objective function. Figure A.3.12 shows comparisons between model predictions using estimated parameter values and experimental data. Note that final M_n and M_w predictions are too high for the thermally initiated polymerization predictions (Figure A.3.12(b), (c), (e), (g), (j), (k) and (n)) and too low for the chemically initiated polymerization predictions.
Rank	Parameter	Initial Value	Final Value
1	k _{fdo} /k _{po}	6.7135x10 ⁻¹	9.8245x10 ⁻¹
2	$(E_a/R)_1$	1.3672×10^4	1.1408x10 ⁴
3	$(E_a/R)_i$	1.1189×10^4	8.2945x10 ³
4	$[(E_a/R)_{fd}-(E_a/R)_p]$	4.5781×10^2	1.1330x10 ³
5	$(E_a/R)_{dDCP}$	1.8362×10^4	1.1666x10 ⁴
6	k _{dBPOo}	1.7508x10 ⁻⁴	4.9155x10 ⁻⁵
7	K _{ref}	2.7500×10^2	2.4732x10 ²
8	А	3.4800x10 ⁻¹	4.4091x10 ⁻¹
9	α _m	1.0000x10 ⁻³	1.4996x10 ⁻³
10	$[(E_a/R)_{tc}-(E_a/R)_p]$	-3.1570×10^3	
11	k ₁₀	3.1863x10 ⁻¹⁰	
12	k _{fmo}	2.0856x10 ⁻¹	
13	k _{io}	8.4641x10 ⁻⁵	
14	k _{dDCPo}	1.5320x10 ⁻⁴	
15	$(E_a/R)_p$	3.9100x10 ³	
16	k _{po}	3.4387×10^2	
17	k _{tco} /k _{po}	3.2159x10 ⁵	
18	$(E_a/R)_{fm}$	6.3770x10 ³	
19	V _{fcrmo}	3.0621x10 ⁻²	
20	$(E_a/R)_{1/-1}$	6.4561x10 ³	
21	E _{cr}	5.0000x10 ³	
22	V_{fpj}	8.3500x10 ⁻¹	
23	f _{io}	7.0000x10 ⁻¹	
24	f ₁₀	7.0000x10 ⁻¹	
25	V _{fmj}	9.1200x10 ⁻¹	
26	δ _c	1.0000x10 ⁻³	
27	α _p	4.8000x10 ⁻⁴	
28	E _{crm}	1.6700×10^3	
29	N	1.75	
30	A _{1/-1}	6.4000x10 ⁴	
31	f ₂₀	7.0000x10 ⁻¹	
32	В	1.0	
33	k _{sDCPo}	6.9861x10 ¹	
34	$(E_a/R)_{sBPO}$	3.6225×10^3	
35	k _{sBPOo}	6.9861x10 ¹	
36	$(E_a/R)_{sDCP}$	3.6225x10 ³	

Table A.3.6. Ranked list of parameters after implementation of transfer-to-monomer reaction and results of parameter estimation Attempt 5.









Figure A.3.12. Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.3.6 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].

A.3.14 Implementation of Transfer-to-Monomer Reaction Starting with Best Parameters Obtained Thus Far

A parameter estimation was attempted after implementation of the transfer-to-monomer reaction. Figure A.3.13 shows model predictions using the parameter values that provide the lowest value of the objective function (Attempt 4), which are shown in the third column of Table A.3.7. The objective function value associated with this model comparison is 108140, higher than before implementation of the transfer-to-monomer reaction (which had an objective function value of 38840). The parameters shown in the third column of Table A.3.7 (as well as Greszta's^[4] values for the transfer to monomer rate coefficients) were used as initial guesses for a subsequent parameter ranking and estimation.









Figure A.3.13. Comparisons between model predictions using the hand tuned values shown in the third column of Table A.3.7 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].

		nation Attemp	10.
Rank	Parameter	Initial Value	Final Value
1	k _{dBPOo}	1.1978x10 ⁻⁴	4.7502x10 ⁻⁴
2	k_{fdo}/k_{po}	7.3606x10 ⁻¹	8.2534x10 ⁻¹
3	$[(E_a/R)_{fd}\text{-}(E_a/R)_p]$	4.5781×10^2	3.5753×10^2
4	$(E_a/R)_i$	1.1189x10 ⁴	9.5801x10 ³
5	$(E_a/R)_1$	1.3672×10^4	$1.2432 x 10^4$
6	А	5.0000x10 ⁻¹	5.0593x10 ⁻¹
7	k _{dDCPo}	1.1131x10 ⁻⁴	8.6781x10 ⁻⁵
8	$(E_a/R)_{dDCP}$	1.7378x10 ⁴	$1.2730 \mathrm{x} 10^4$
9	$\mathbf{V}_{\mathrm{fmj}}$	9.1200x10 ⁻¹	9.9898x10 ⁻¹
10	α _m	1.0000x10 ⁻³	
11	α _p	4.8000x10 ⁻⁴	
12	k ₁₀	3.1863x10 ⁻¹⁰	
13	$(E_a/R)_{fm}$	6.3770x10 ³	
14	$(E_a/R)_p$	3.9100x10 ³	
15	$(E_a/R)_{1/-1}$	6.4561x10 ³	
16	k _{po}	3.4387x10 ²	
17	$[(E_a/R)_{tc}-(E_a/R)_p]$	-3.1570×10^3	
18	k _{io}	8.4641x10 ⁻⁵	
19	k_{tco}/k_{po}	3.2159x10 ⁵	
20	K _{ref}	9.5000x10 ²	
21	V _{fcrmo}	3.0621x10 ⁻²	
22	V_{fpj}	8.3500x10 ⁻¹	
23	k _{fmo}	2.0856x10 ⁻¹	
24	f ₁₀	7.0000x10 ⁻¹	
25	f ₂₀	7.0000x10 ⁻¹	
26	f _{io}	7.0000x10 ⁻¹	
27	n	1.75	
28	В	1.0	
29	δ_{c}	1.0000x10 ⁻³	
30	A _{1/-1}	6.4000x10 ⁴	
31	E _{crm}	1.6700×10^3	

Table A.3.7. Ranked list of parameters after implementation of transfer-to-monomer reaction using estimated parameter values from Attempt 4 as initial guesses and results of parameter estimation Attempt 6.

A.3.15 Parameter Ranking and Estimation Results: Attempt 6 using Complete Literature Data Set

Figure A.3.14 shows model prediction after implementation of the transfer-to-monomer reaction and subsequent parameter estimation. Wu's method indicated that nine parameters should be estimated, which resulted in a decrease in the value of the objective function from 108140 to 34560 which was the best value obtained so far. Values of the nine estimated parameters are shown in the last column of Table A.3.7. Conversion predictions of thermally initiated polymerization data are good, and M_n and M_w predictions show good trends, although final values are too high. There is some mismatch in the prediction of initial polymerization rates using DCP and BPO initiators, as well as the initial M_n and M_w , however final conversion, molecular weight averages and MWD predictions are good. Note that the transfer to monomer rate coefficients were not among the top nine parameters selected for estimation even though incorporation of transfer to monomer resulted in a marked improvement in the value of the objective function (38840 to 34560). This result led us to re-examine the scaling factor associated with these parameters.









Figure A.3.14. Comparisons between model predictions using the estimated parameter values shown in the last column of Table A.2.7 (—) and conversion (\Diamond , Δ), M_n (\Diamond), M_w (\Box) and MWD (\Diamond) data collected in thermal initiation (TI) and chemical initiated (CI) styrene polymerization studies. (a) 100 °C, TI^[1]; (b) 100 °C, TI^[1]; (c) 100 °C, TI^[1]; (d) 120 °C, TI^[1]; (e) 120 °C, TI^[1]; (f) 140 °C, TI^[1]; (g) 140 °C, TI^[1]; (h) 150 °C, TI^[2]; (i) 150 °C, TI^[2]; (j) 160 °C, TI (Δ)^[1], (\Diamond)^[2]; (k) 160 °C, TI^[2]; (l) 165 °C, TI^[1]; (m) 170°C, TI^[2]; (n) 170°C, TI^[2]; (o) 120 °C, CI [DCP, 4000 ppm]^[2]; (p) 120 °C, CI [DCP, 4000 ppm]^[2], (q) 130 °C, CI [DCP, 4000 ppm]^[2]; (r) 130 °C, CI [DCP, 4000 ppm]^[2]; (s) 130 °C, CI [DCP, 4000 ppm]^[2]; (v) 140 °C, CI [DCP, 4000 ppm]^[2]; (w) 150 °C, CI [DCP, 4000 ppm]^[2]; (x) 150 °C, CI [DCP, 4000 ppm]^[2]; (y) 90 °C, CI [BPO, 3050 ppm]^[3]; (z) 90 °C, CI [BPO, 3050 ppm]^[3].

A.3.16 Parameter Ranking and Estimation Results: Attempt 7 using Complete Literature Data Set

Upon re-examination of the scaling factors associated with the transfer-to-monomer reaction, it was decided that they could be increased to account for a larger proportion of chain transfer attributable to monomer. The upper bound for k_{fmo} was set to a value which results in approximately 30 % of the transfer reactions being attributable to transfer to monomer rather than transfer to adduct and the scaling factor used for parameter rank was increased accordingly. Parameter ranking resulted in a list very similar to the one shown in Table A.3.7 but with k_{fmo} ranked at the top of the list. Parameter estimation was then performed using the parameter values in Table A.3.7 as initial guesses which resulted in a decrease in the value of the objective function from 108140 to 67471. Note that this objective function value is much worse than 34560 which obtained in Attempt 6. Also note that Wu's method indicated that only the top parameter, k_{fmo} , should be estimated. The high objective function value indicates that the parameter estimation became caught in a local minimum after estimating the value of k_{fmo} and could not find better values of the remaining parameters. Predictions of conversion, M_n, M_w and MWD are worse than those resulting from Attempt 6 and are therefore not shown.

A.3.17 References

- [1] A.W. Hui, A.E. Hamielec, *Journal of Applied Polymer Science*, **1972**, *16*, 749.
- [2] C. Kotoulas, A. Krallis, P. Pladis, C. Kiparissides, *Macromolecular Chemistry and Physics*, **2003**, *204*, 1305.
- [3] M.A. Villalobos, A.E. Hamielec, P.E. Wood, *Journal of Applied Polymer Science*, **1993**, *50*, 327.
- [4] D. Greszta, K. Matyjaszewski, *Macromolecules*, **1996**, *29*, 7661.