Identification and Control
This book is an ambitious attempt to bridge the infamous gap between theory and practice in control. The book has ten chapters, written by seasoned researchers from all over the world. It is organized in four parts: Large-scale Problems, Aerospace, Vision and Sound and Electromechanical, and covers a very wide range of problems from chemical reactors to magnetic bearings. In spite of the wide diversity of topics and authors a coherent presentation is obtained by a uniform organization imposed by the editors. Each chapter begins with a brief summary of the theory and a description of the application, followed by results of simulations or experiments and conclusions. The problem descriptions and the discussions about the relevance of the theory are more detailed than presentations normally found in papers. The book is a nice complement to traditional textbooks and the wide range of topics illustrate the richness and ubiquity of identification and control.

Santa Barbara, California, USA

March 2007

Karl Johan Åström
System theory, in particular, automatic control and system identification have experienced a fast evolution in the past decades. Many new methods have been developed, performance requirements in traditional engineering areas have significantly increased and new and more demanding applications in other areas of engineering and science have appeared. Many textbooks have been written that present the relevant theory and sometimes “practical” examples to which the theory has been applied. Other books focus directly on the practical issues involved, leaving the theory out. However, there is still an important gap between theory and its application to practical problems. Engineering decisions are usually made without the complete assessment of existing theoretical tools. Many times, the key to the applicability of new methods is based on such decisions. Hence, a problem appears when either theory is lacking – it trails behind the practical issues, or when engineering decisions are taken without the knowledge of recent theoretical developments.

Usually the theory/practice gap is covered by extensive simulations and/or experimental testing. There are very few (if any) situations in which the theory “fits” the practical application without any extra modification. This gap is even more important in critical situations such as nuclear plants and space applications, where the mismatch between theory and practice could lead to dangerous or disastrous scenarios. Nevertheless, this gap is the motor that keeps theoreticians and practitioners active in developing new techniques and applying them in all areas of engineering. The purpose of this book is to present some examples of this gap and in this way serve as a reference, where new applied research areas are pointed out.

All chapters are written by textbook authors involved in “real world” applications from different areas of engineering: acoustics, aerospace, chemical, computer vision, electromechanical, industrial and mining. The chapters are organized with a similar format: (1) a brief theoretical background section with references to previous works; (2) the description of the application(s); (3) a presentation of simulations and/or experimental results, and (4) conclusions highlighting the discrepancy between theory and practice. The latter is what distinguishes this book from others: the gap is deliberately exposed, not hidden. Furthermore, in each chapter the complete analysis and
design process is covered, describing practical issues and decisions that accomodate
the existing theory to the particular problem.

The book will be useful for engineers facing complex applications and willing
to use recent methods of identification and control in solving them, in order to take
sound engineering decisions. In addition, applied researchers looking for areas in
which to contribute in reducing the theory/practice gap and exploring practical issues
should also benefit greatly from it.

The chapters describe how different identification and control techniques are ap-
plied to a wide variety of engineering applications. The identification methods go
from parametric identification of linear and nonlinear models, to robust set member-
ship identification and model (in)validation. Control techniques range from stochas-
tic optimal control to model predictive or robust $\mathcal{H}_\infty$ and $\mu$-synthesis control. Also,
fault tolerant and linear parameter varying (LPV) control, and the recent area of hy-
brid systems control techniques, have been used. Among the applications we can
mention: mine planning, polymerization reactors, a copper foundry process, and the
sewer network of Barcelona. Also, some electromechanical processes such as active
transmission and suspension, and a magnetic-bearing rotor appear. Computer vision,
aerospace applications like the NASA-JPL flexible structure or aeroservoelasticity in
the F18 aircraft and acoustic-noise attenuation, are also included.

Finally, we would like to thank all the authors who contributed to this book, for
producing an excellent collection of high-quality technical material. We would also
like to thank Springer UK personnel, particularly Oliver Jackson, who helped us
greatly in the development of this project, and our colleague Ari Ingimundarson for
refining part of this text.

Terrassa, Barcelona, Spain, March 2007

Ricardo S. Sánchez Peña
Joseba Quevedo Casín
Vicenç Puig Cayuela
Contents

Part I Large-scale Problems

1 Identification and Control of Polymerization Reactors
Eric J. Hukkanen, Jeremy G. VanAntwerp, Richard D. Braatz ............... 3
1.1 Background ............................................................ 3
1.2 Free-radical Polymerization ......................................... 5
1.3 Simulation and Experimental Results .............................. 13
1.4 Discrepancies Between Theory and Experimental Results ............. 33
References ..................................................................... 39

2 Open-cut Mine Planning via Closed-loop Receding-horizon Optimal Control
Cristian R. Rojas, Graham C. Goodwin, María M. Seron, Meimei Zhang ...... 43
2.1 Background ............................................................. 43
2.2 Experiment Description ............................................... 45
2.3 Simulation Results ...................................................... 50
2.4 Discrepancy Between Theory and Experiments .......................... 56
References ..................................................................... 60

3 Energy Saving in a Copper Smelter by means of Model Predictive Control
Carlos Bordons, Manuel R. Arahal, Eduardo F. Camacho, José M. Tejera ...... 63
3.1 Background ............................................................. 63
3.2 Experiment Description ............................................... 66
3.3 Results ................................................................. 76
3.4 Discrepancies between Theory and Practice ............................ 84
References ..................................................................... 85

4 On Hybrid Model Predictive Control of Sewer Networks
Carlos Ocampo-Martinez, Alberto Bemporad, Ari Ingimundarson, Vicenç Puig Cayuela ................................................................. 87
4.1 Background ............................................................. 87
4.2 Hybrid Modeling and Control of Sewage Systems ......................... 90
4.3 Simulation and Results .................................................. 102
4.4 Discrepancies and Misfits .............................................. 107
References ................................................................. 111

Part II Aerospace

5 Nonlinear System Identification of Aeroelastic Systems:
A Structure-detection Approach
Sunil L. Kukreja, Martin J. Brenner ........................................ 117
5.1 Background ........................................................................ 117
5.2 Application I ..................................................................... 125
5.3 LASSO Applications .......................................................... 136
5.4 Concluding Remarks .......................................................... 142
References ............................................................................. 142

6 Modeling and Control of Flexible Structures in Frequency Domain
Luis Alvergue, Jie Chen, Guoxiang Gu ........................................ 147
6.1 Background ........................................................................ 147
6.2 Robust Stabilization ............................................................ 148
6.3 Robust Modeling ................................................................. 153
6.4 Simulation Results for the JPL Flexible Structure ..................... 158
6.5 Conclusion ........................................................................... 163
References ............................................................................. 164

Part III Vision and Sound

7 Robust Identification and Model (In)Validation of Active-vision
Systems
Tamer Inanc, Mario Sznaier, Octavia Camps .................................. 167
7.1 Background ........................................................................ 167
7.2 Description of Application Example ...................................... 175
7.3 Experimental Results ........................................................... 178
7.4 Discrepancies/Misfits between Theory and Experimental Results .... 183
7.5 Conclusions ........................................................................ 195
References ............................................................................. 198

8 Identification and Control Structure Design in Active (Acoustic) Noise
Control
Miquel A. Cugueró, Bernardo Morcego, Ricardo S. Sánchez Peña ........ 203
8.1 Background ........................................................................ 203
8.2 Acoustic-noise Experimental Setup ........................................ 220
8.3 Identification and Control Experiments .................................... 224
8.4 Compromises and Discrepancies between Theory and Practice ........ 239
References ............................................................................. 242
Part IV Electromechanical

9 Iterative Identification and Control Design: Methodology and Applications
Pedro Albertos, Alicia Esparza, Antonio Sala ........................................... 247
9.1 Background .................................................................................................. 247
9.2 Description of the Applications ................................................................. 252
9.3 Simulations and Experimental Examples .................................................. 255
9.4 Discrepancies/Misfits between Theory and Experimental Results ............ 271
References ...................................................................................................... 274

10 Classical, Robust and LPV Control of a Magnetic-bearing Experiment
Alejandro S. Ghersin, Roy S. Smith, Ricardo S. Sánchez Peña .......................... 277
10.1 Introduction and Background ................................................................. 278
10.2 The Magnetic-bearing Experiment ......................................................... 292
10.3 Control and Simulation Results ............................................................... 309
10.4 Discrepancies between Theory and Practice .......................................... 320
References ...................................................................................................... 323

Index ................................................................................................................ 327
List of Contributors

Pedro Albertos
Universidad Politécnica de Valencia,
Dept. Systems Engineering and Control,
P.O. Box. 22012, E-46071, Valencia,
Spain
pedro@aii.upv.es

Luis Alvergue
Louisiana State University,
Department of Electrical and Computer
Engineering,
Baton Rouge, LA 70803-5901, USA
lalver1@lsu.edu

Manuel R. Arahal
Universidad de Sevilla,
Departamento de Ingeniería de
Sistemas y Automática,
Sevilla, Spain
arahal@esi.us.es

Alberto Bemporad
Università di Siena,
Dipartimento di Ingegneria
dell’Informazione
Via Roma 56, I-53100
Siena, Italy
bemporad@dii.unisi.it

Carlos Bordons
Universidad de Sevilla,

Departamento de Ingeniería de
Sistemas y Automática,
Sevilla, Spain
bordons@esi.us.es

Richard D. Braatz
University of Illinois at Urbana-
Champaign,
Department of Chemical and Biomolec-
ular Engineering,
293 Roger Adams Laboratory, Box C-3,
600 South Mathews Avenue, Urbana, IL
61801, USA
braatz@uiuc.edu

Martin J. Brenner
NASA Dryden Flight Research Center,
Aerostructures Branch, Edwards, CA,
USA
Martin.J.Brenner@nasa.gov

Eduardo F. Camacho
Universidad de Sevilla,
Departamento de Ingeniería de
Sistemas y Automática,
Sevilla, Spain
eduardo@esi.us.es

Octavia Camps
Northeastern University,
ECE Department,
Boston, MA 02115, USA
camps@ece.neu.edu
List of Contributors

Jie Chen
University of California,
Department of Electrical Engineering,
Riverside, CA 92521, USA
jchen@ee.ucr.edu

Miquel A. Cugueró
Universitat Politècnica de Catalunya,
Sistemes Avançats de Control,
Rbla. Sant Nebridi 10,
Terrassa, 08222 Barcelona, Spain
miquel.angel.cuguero@upc.edu

Alicia Esparza
Universidad Politécnica de Valencia,
Dept. Systems Engineering and Control,
P.O. Box. 22012, E-46071, Valencia, Spain
alespei@isa.upv.es

Alejandro S. Ghersin
Universidad Nacional de Quilmes,
Ingeniería en Automatización y Control,
and Universidad de Buenos Aires,
Facultad de Ingeniería,
Buenos Aires, Argentina
aghersin@unq.edu.ar

Graham Goodwin
The University of Newcastle,
Centre for Complex Dynamic Systems and Control,
School of Electrical Engineering and Computer Science,
Callaghan NSW 2308, Australia
graham.goodwin@newcastle.edu.au

Guoxiang Gu
Louisiana State University,
Department of Electrical and Computer Engineering,
Baton Rouge, LA 70803-5901, USA
ggu@lsu.edu

Eric J. Hukkanen
Real-Time Analytics,
Mettler-Toledo AutoChem, Inc.,
14833 NE 87th Street, Redmon, WA 98052, USA
eric.hukkanen@mt.com

Tamer Inanc
University of Louisville,
ECE Department,
Louisville, KY 40292, USA
t.inanc@louisville.edu

Ari Ingimundarson
Universitat Politècnica de Catalunya,
Sistemes Avançats de Control,
Rbla. Sant Nebridi 10,
Terrassa, 08222 Barcelona, Spain
ari.ingimundarson@upc.edu

Sunil L. Kukreja
NASA Dryden Flight Research Center,
Aerostructures Branch, Edwards, CA, USA
Sunil.Kukreja@nasa.gov

Bernardo Morcego
Universitat Politècnica de Catalunya,
Sistemes Avançats de Control,
Rbla. Sant Nebridi 10,
Terrassa, 08222 Barcelona, Spain
bernado.morcego@upc.edu

Carlos Ocampo Martínez
Universitat Politècnica de Catalunya,
Sistemes Avançats de Control,
Rbla. Sant Nebridi 10,
Terrassa, 08222 Barcelona, Spain
carlos.ocampo@upc.edu

Vicenç Puig Cayuela
Universitat Politècnica de Catalunya,
Sistemes Avançats de Control,
Rbla. Sant Nebridi 10,
Terrassa, 08222 Barcelona, Spain
vicenc.puig@upc.edu
Cristian R. Rojas  
The University of Newcastle,  
Centre for Complex Dynamic Systems and Control,  
School of Electrical Engineering and Computer Science,  
Callaghan NSW 2308, Australia  
cristian.rojas@studentmail.newcastle.edu.au

Antonio Sala  
Universidad Politécnica de Valencia,  
Dept. Systems Engineering and Control,  
P.O. Box. 22012, E-46071, Valencia, Spain  
asala@isa.upv.es

Ricardo S. Sánchez Peña  
ICREA and Universitat Politècnica de Catalunya,  
Sistemes Avançats de Control,  
Rbla. Sant Nebridi 10, Terrassa, 08222 Barcelona, Spain  
ricardo.sanchez-pena@upc.edu

María M. Seron  
The University of Newcastle,  
Centre for Complex Dynamic Systems and Control,  
School of Electrical Engineering and Computer Science,  
Callaghan NSW 2308, Australia  
maria.seron@newcastle.edu.au

Roy S. Smith  
University of California,  
Department of Electrical and Computer Engineering  
Santa Barbara, CA 93106, USA  
roy@ece.ucsb.edu

Mario Sznaier  
Northeastern University,  
ECE Department,  
Boston, MA 02115, USA  
msznaier@ece.neu.edu

José M. Tejera  
Atlantic Copper,  
Departamento de Servicios Generales, Electricidad e Instrumentación, Huelva, Spain.  
Jose-Maria-Tejera@fmi.com

Jeremy G. VanAntwerp  
Calvin College, Department of Engineering,  
1726 Knollcrest Circle, Grand Rapids, MI 49546, USA  
jva@calvin.edu

Meimei Zhang  
The University of Newcastle,  
Centre for Complex Dynamic Systems and Control,  
School of Electrical Engineering and Computer Science,  
Callaghan NSW 2308, Australia  
MeiMei.Zhang@BHPBilliton.com
Part I

Large-scale Problems
Identification and Control of Polymerization Reactors

Eric J. Hukkanen\textsuperscript{1}, Jeremy G. VanAntwerp\textsuperscript{2}, and Richard D. Braatz\textsuperscript{3}

\textsuperscript{1} Real-Time Analytics, Mettler-Toledo AutoChem, Inc., 14833 NE 87th Street, Redmond, WA 98052, USA eric.hukkanen@mt.com
\textsuperscript{2} Calvin College, Department of Engineering, 1726 Knollcrest Circle, Grand Rapids, MI 49546, USA jva@calvin.edu
\textsuperscript{3} University of Illinois at Urbana-Champaign, Department of Chemical and Biomolecular Engineering, 293 Roger Adams Laboratory, Box C-3, 600 South Mathews Avenue, Urbana, IL 61801, USA braatz@uiuc.edu

Summary. This chapter considers the identification and control of free-radical polymerization reactors. A discussion of the modeling and simulation of such reactors is followed by an optimal control study that demonstrates the potential of optimal control of the molecular-weight distribution based on mechanistic models. Achieving this potential in a batch reactor requires an accurate estimation of the free-radical polymerization kinetic parameters. The remainder of the chapter describes an experimental investigation of the free-radical polymerization of methyl methacrylate, in which modern sensing techniques are used to estimate kinetic parameters. The monomer conversion is measured using inline ATR-FTIR spectroscopy and robust chemometrics, and the molecular-weight distribution is measured by gas-permeation chromatography. The resulting parameter estimates and confidence intervals are used to discuss the importance of various reactions in the free-radical polymerization reaction mechanism. Discrepancies between theory and experiments are discussed.

1.1 Background

Accurate mechanistic models for predicting the molecular-weight distribution are necessary for effective design and control of free-radical polymerization reactors. Many studies have been conducted to identify mechanistic models for free-radical polymerization ([8, 9, 11–17, 20, 22, 23, 26–28]). The accuracy of the estimates of the kinetic parameters is directly related to the accuracy and reliability of the sensors available for measuring the monomer conversion and molecular-weight properties. This chapter makes use of two sensing technologies, \textit{in situ} attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy and gel-permeation chromatography, for kinetic-parameter estimation in polymerization reactors. The chapter also considers methods by which models for such processes can be simulated, as a necessary first step to model identification, and considers the use of such models for control.

The first sensing technology is enabled by the availability of midrange infrared transmitting optical fibers [21]. A significant advantage of ATR-FTIR spectroscopy over most other methods for concentration measurement is the ability to provide simultaneous measurement for multiple chemical species. This is useful, for example, for measuring the monomer concentration in a polymerization reactor independent of the concentrations of dimers, trimers, etc.
In ATR-FTIR spectroscopy, the infrared spectrum is characteristic of the vibrational structure of the substance in immediate contact with the ATR immersion probe. The ATR-FTIR probe, coupled with robust chemometrics, is used to monitor the conversion of monomer during experiments. The second sensing technology, gel-permeation chromatography (GPC), measures the molecular-weight distribution (MWD), which is the polymer property that determines its end-use characteristics [21]. First, a calibration curve is constructed using narrowly distributed polymer samples of known molecular-weight. Then this calibration curve is used offline to determine the MWD over the course of a reaction.

The specific polymerization under investigation is the free-radical polymerization of methyl methacrylate. Various assumptions have been used to develop mechanistic models for this process. It has been assumed that monomer transfer, $k_{trm}$, and/or termination by combination, $k_{tc}^o$, do not significantly influence the polymerization process [8, 11–16, 22, 27, 28]. The results of a literature search [8, 9, 12, 14, 17, 20, 22, 23, 26, 27] of kinetic parameters used for modeling methyl methacrylate bulk polymerization are summarized in Table 1.1. The large variability of the values of the kinetic parameters may be partly due to the inclusion/exclusion of $k_{trm}$ and $k_{tc}^o$. Also, past studies usually fit kinetic parameters based only on a measurement of the monomer conversion over time for a small number of batch polymerizations, and this is very limited information for estimating the values of multiple kinetic parameters, as we will see later in this study. For control purposes, it is necessary to have an estimate of the error in the parameter estimates. Most papers do not provide any uncertainty assessment of their parameter estimates. In this chapter, monomer conversion profiles (as measured by in situ ATR-FTIR spectroscopy [19]) and average molecular-weight properties (determined by offline gel-permeation chromatography) are used to determine kinetic parameters for the free-radical polymerization of methyl methacrylate (MMA) with benzoyl peroxide (BPO) initiator. 95% confidence intervals are reported with the parameter estimates.

The next section describes the polymerization kinetic model, model simulation, description of the experimental system, and formulation of the parameter estimation and optimal control problems. This is followed by simulation-model verification and an evaluation of the potential of optimal control of the molecular-weight distribution in free-radical polymerization. Next, the kinetic parameters needed for optimal control design are experimentally determined. The chapter ends with a discussion of discrepancies between the experimental data and the model outputs obtained with the estimated kinetic parameters.

Table 1.1. Kinetic parameter estimates (along with 95% confidence regions) obtained from literature values

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Literature values</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$</td>
<td>0.10–1.0</td>
<td>—</td>
</tr>
<tr>
<td>$k_{trm}$</td>
<td>1.6 ± 7.8</td>
<td>[L mol$^{-1}$ min$^{-1}$]</td>
</tr>
<tr>
<td>$k_{tc}^o \times 10^{-9}$</td>
<td>1.8 ± 0.8</td>
<td>[L mol$^{-1}$ min$^{-1}$]</td>
</tr>
<tr>
<td>$k_{tc}^p \times 10^{-8}$</td>
<td>7.6 ± 1.1</td>
<td>[L mol$^{-1}$ min$^{-1}$]</td>
</tr>
<tr>
<td>$k_{tc}^o \times 10^{-4}$</td>
<td>3.2 ± 0.7</td>
<td>[L mol$^{-1}$ min$^{-1}$]</td>
</tr>
</tbody>
</table>
1.2 Free-radical Polymerization

This section describes mechanistic modeling of a free-radical bulk polymerization reactor and an algorithm for the direct simulation of the molecular-weight distribution. It is straightforward to revise the model to treat solution, suspension, or emulsion polymerization, or anionic or cationic polymerization. Subsequent sections use this mechanistic model for parameter estimation and optimal control.

1.2.1 Kinetic Model

The reaction mechanism with reaction rates for free-radical polymerization with a single monomer and initiator are

\[ I_2 \xrightarrow{k_d} 2I \cdot \quad r_d = 2f k_d [I_2] \quad \text{initiator decomposition} \]

\[ I \cdot + M \xrightarrow{k_i} P_1 \quad r_i = k_i [M] [I \cdot] \quad \text{initiation} \]

\[ P_n + M \xrightarrow{k_p} P_{n+1} \quad r_p = k_p [M] [P_n] \quad \text{propagation} \]

\[ P_n + M \xrightarrow{k_{trm}} D_n + P_1 \quad r_{trm} = k_{trm} [M] [P_n] \quad \text{monomer transfer} \]

\[ P_n + P_m \xrightarrow{k_{tc}} D_{n+m} \quad r_{tc} = k_{tc} [P_m] [P_n] \quad \text{termination by combination} \]

\[ P_n + P_m \xrightarrow{k_{td}} D_n + D_m \quad r_{td} = k_{td} [P_m] [P_n] \quad \text{termination by disproportionation} \]

It is straightforward to generalize the mechanism to include chain-transfer and solvent-transfer reactions and multiple monomers and initiators.

The molar balances for a well-mixed batch reactor are, for initiator decomposition

\[ \frac{1}{V} \frac{d}{dt} ([I_2]V) = -k_d [I_2] \quad (1.1) \]

free-radical concentration

\[ \frac{1}{V} \frac{d}{dt} ([I \cdot]V) = -k_i [I \cdot][M] + 2f k_d [I_2] \quad (1.2) \]

monomer concentration

\[ \frac{1}{V} \frac{d}{dt} ([M]V) = -k_i [I \cdot][M] - (k_p + k_{trm}) [M] \sum_{j=1}^{\infty} [P_j] \quad (1.3) \]

live polymer chains

\[ \frac{1}{V} \frac{d}{dt} ([P_1]V) = k_i [I \cdot][M] - k_p [M][P_1] - k_{trm} [M] \left( [P_1] - \sum_{j=1}^{\infty} [P_j] \right) \]

\[ - (k_{tc} + k_{td}) [P_1] \sum_{j=1}^{\infty} [P_j] \quad (1.4) \]

\[ \frac{1}{V} \frac{d}{dt} ([P_m]V) = k_p [M] ([P_{m-1}] - [P_m]) - k_{trm} [M][P_m] \quad (1.5) \]

\[ - (k_{tc} + k_{td}) [P_m] \sum_{j=1}^{\infty} [P_j] \quad \text{for } m = 2, \cdots, n \]
and dead polymer chains

\[
\frac{1}{V} \frac{d}{dt} ([M] [P]) = \sum_{j=1}^{\infty} [P]_{j} + \frac{1}{2} k_{tc} \sum_{j=1}^{m-1} [P]_{j} [P_{m-j}] 
\]

for \( m = 2, \ldots, n \)

The parameters \( k_{d}, k_{i}, k_{p}, k_{trm}, k_{tc} \), and \( k_{td} \) are rate constants and \( f \) is the initiator efficiency. The short average lifetime \((<< 1 \text{ s})\) of an initiator radical molecule, \( I \cdot \), implies that the quasisteady-state approximation can be applied:

\[
\frac{1}{V} \frac{d}{dt} ([I \cdot] [V]) = 0
\]

and

\[
k_{i} [I \cdot] [M] = 2 f k_{d} [I_{2}]
\]

The total concentrations of live polymer molecules and monomer are

\[
[P] = \sum_{j=1}^{\infty} [P]_{j}
\]

\[
[M] = [M_{o}] (1 - x) \frac{1}{1 + \varepsilon x}
\]

where \( x \) is the conversion and \( \varepsilon \) is the volume-contraction factor

\[
\varepsilon = \frac{\rho_{m}(T) - \rho_{p}(T)}{\rho_{p}(T)}
\]

that takes into account the density differences between the polymer and monomer. Initially, the reactor consists of pure monomer. Throughout the reaction, the volume of the reactant/product mixture changes according to

\[
V = V_{0}(1 + \varepsilon x)
\]

\[
\frac{dV}{dt} = V_{0} \varepsilon \frac{dx}{dt}
\]

In this work, the gel effect or “Trommsdorf effect” is accounted for using the free-volume correlation [25]. The void volume in a monomer/polymer solution is defined as the free volume. As conversion increases, the free volume decreases. Established methods are implemented to account for the decrease in propagation and termination due to strong diffusion limitations. The overall termination rate, \( k_{t} \), takes the form

\[
k_{t} = k_{td} + k_{tc}
\]

\[
k_{t} = k_{t}^g g_{t}
\]

where

\[
g_{t} = \begin{cases} 
0.10575 e^{17.15 \nu_{f} - 0.01715(T - 273.15)} & \nu_{f} > \nu_{f,cr} \\
0.23 \times 10^{-5} e^{75 \nu_{f}} & \nu_{f} \leq \nu_{f,cr}
\end{cases}
\]

and the propagation rate takes the form

\[
k_{p} = k_{p}^g g_{p}
\]

\[
g_{p} = \begin{cases} 
1 & \nu_{f} > \nu_{f,cr} \\
0.71 \times 10^{-4} e^{71.53 \nu_{f}} & \nu_{f} \leq \nu_{f,cr}
\end{cases}
\]
The free volume, $\nu_f$, is defined by

$$\nu_f = \phi_m \nu_{f,m} + \phi_p \nu_{f,p}$$  \hspace{1cm} (1.19)

where $\phi_m$ and $\phi_p$ are the volume fractions of monomer and polymer, respectively, and the monomer $\nu_{f,m}$ and polymer $\nu_{f,p}$ free volumes are defined by

$$\nu_{f,m} = 0.025 + 0.001(T - 167)$$  \hspace{1cm} (1.20)
$$\nu_{f,p} = 0.025 + 0.00048(T - 387)$$  \hspace{1cm} (1.21)

The critical free volume, $\nu_{f,cr}$, is defined by

$$\nu_{f,cr} = 0.1856 - 2.965 \times 10^{-4}(T - 273.15)$$  \hspace{1cm} (1.22)

This free-volume model is adapted from [25] and has been used in several investigations [11–13, 20, 26].

### 1.2.2 Model Simulation

This section describes how the kinetic model was simulated and presents the moment equation method that was used to verify the accuracy of the simulation results.

#### Moment equations

The moments are defined by

$$\lambda_i = \sum_{j=1}^{\infty} j^i[P_j]$$  \hspace{1cm} (1.23)

for live (radical) polymer chains and

$$\mu_i = \sum_{j=2}^{\infty} j^i[D_j]$$  \hspace{1cm} (1.24)

for dead polymer chains, where $i$ is an integer. The infinite set of molar balance equations can be used to derive a finite number of ordinary different equations (ODEs) by using the relationships

$$\sum_{j=1}^{\infty} \frac{d}{dt} \left( j^i[P_j] \right) = \frac{d\lambda_i}{dt} \text{ for } i = 0, 1, 2$$  \hspace{1cm} (1.25)

and

$$\sum_{j=2}^{\infty} \frac{d}{dt} \left( j^i[D_j] \right) = \frac{d\mu_i}{dt} \text{ for } i = 0, 1, 2$$  \hspace{1cm} (1.26)

The resulting finite set of ODEs are

$$\frac{d[I_2]}{dt} = -\left( k_d + \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt} \right) [I_2]$$  \hspace{1cm} (1.27)

$$\frac{dx}{dt} = \frac{2f k_d [I_2]}{[M_w]} (1 + \varepsilon x) + (k_p + k_{trm}) (1 - x) \lambda_0$$  \hspace{1cm} (1.28)
\[ \frac{d\lambda_0}{dt} = 2f k_d[I_2] - (k_{td} + k_{tc}) \lambda_0^2 - \frac{\varepsilon \lambda_0}{1 + \varepsilon x} \frac{dx}{dt} \] (1.29)

\[ \frac{d\lambda_1}{dt} = 2f k_d[I_2] + k_p[M] \lambda_0 + k_{trm}[M] (\lambda_0 - \lambda_1) \\
- (k_{td} + k_{tc}) \lambda_0 \lambda_1 - \frac{\varepsilon \lambda_1}{1 + \varepsilon x} \frac{dx}{dt} \] (1.30)

\[ \frac{d\lambda_2}{dt} = 2f k_d[I_2] + k_p[M] (2\lambda_1 + \lambda_0) + k_{trm}[M] (\lambda_0 - \lambda_2) \\
- (k_{td} + k_{tc}) \lambda_0 \lambda_2 - \frac{\varepsilon \lambda_2}{1 + \varepsilon x} \frac{dx}{dt} \] (1.31)

\[ \frac{d\mu_0}{dt} = k_{trm}[M] \lambda_0 + \left( k_{td} + \frac{1}{2} k_{tc} \right) \lambda_0^2 - \frac{\varepsilon \mu_0}{1 + \varepsilon x} \frac{dx}{dt} \] (1.32)

\[ \frac{d\mu_1}{dt} = k_{trm}[M] \lambda_1 + (k_{td} + k_{tc}) \lambda_0 \lambda_1 - \frac{\varepsilon \mu_1}{1 + \varepsilon x} \frac{dx}{dt} \] (1.33)

\[ \frac{d\mu_2}{dt} = k_{trm}[M] \lambda_2 + k_{td} \lambda_0 \lambda_2 + k_{tc} \left( \lambda_0 \lambda_2 + \lambda_1^2 \right) - \frac{\varepsilon \mu_2}{1 + \varepsilon x} \frac{dx}{dt} \] (1.34)

with initial conditions

\[ [I_2](0) = [I_{2o}] \] (1.35)

\[ x(0) = 0 \] (1.36)

\[ \lambda_i(0) = \mu_i(0) = 0, \quad \text{for } i = 0, 1, 2 \] (1.37)

The polymer product is commonly characterized by the number-average molecular-weight, \( \bar{M}_n \), weight-average molecular-weight, \( \bar{M}_w \), and polydispersity, PD. These product quality variables can be computed from the moments of live and dead polymer chains:

\[ \bar{M}_n = M_w \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0} \] (1.38)

\[ \bar{M}_w = M_w \frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1} \] (1.39)

\[ \text{PD} = \frac{\bar{M}_w}{\bar{M}_n} \] (1.40)

where \( M_w \) is the molecular-weight of the monomer. The above system of ODEs can be solved using any stiff solver such as DASSL [24] or VODE [5].

**Simulation of the Molecular-weight Distribution**

Typically, the molecular-weight distribution (MWD) is simulated using stochastic codes, which are time consuming. Here, the full MWD is simulated in less than 10 min per simulation run. The above molar balances are directly integrated using parallel CVODE [1, 6, 7, 10, 31]. The maximum number of ODEs was determined experimentally by gel-permeation chromatography (GPC), which was double-checked at the end of the simulation to confirm that the live and dead polymer concentrations at the largest chain lengths were negligible. The user selects the number of processors and the maximum number of ODEs allowed on each processor, and specifies which equations are on each processor. The parallel CVODE software...
handles all details of the integration including parallelization among multiple processors. The user decides how to balance the computations among the processors. All communications between processors are handled using the message-passing interface (MPI) [18], using the basic MPI_SEND, MPI_RECV, and MPI_BCAST commands. For a more indepth description of the architecture of the parallel CVODE algorithm, the reader is referred to [1, 6, 7, 10, 31].

As the average lifetime of live polymer chains is very short, the quasisteady-state approximation (QSSA) was applied, which greatly reduces the stiffness:

\[
\frac{1}{V} \frac{d}{dt} \langle [P_m] V \rangle = 0, \quad \text{for } m = 1, \cdots, \infty
\]  

(1.41)

Applying the QSSA reduces the stiffness to \( \sim 10^4 \), which is significantly more well behaved numerically. This leads to the system of ODEs solved by parallel CVODE:

\[
\frac{d[I_2]}{dt} = -\left( k_d + \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt} \right) [I_2] 
\]  

(1.42)

\[
\frac{dx}{dt} = \frac{2f k_d [I_2] (1 + \varepsilon x)}{[M_o]} + (k_p + k_{trm}) (1 - x) [P] 
\]  

(1.43)

\[
\frac{d[P]}{dt} = 2f k_d [I_2] - (k_{td} + k_{tc}) \lambda_0^2 - \frac{\varepsilon \lambda_0}{1 + \varepsilon x} \frac{dx}{dt} 
\]  

(1.44)

\[
[P_1] = \frac{2f k_d [I_2] + k_{trm} [M][P]}{(k_p + k_{trm}) [M] + (k_{td} + k_{tc}) [P] + \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt}} 
\]  

(1.45)

\[
[P_2] = \frac{k_p [M][P_1]}{(k_p + k_{trm}) [M] + (k_{td} + k_{tc}) [P] + \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt}} 
\]  

(1.46)

\[
\vdots 
\]

\[
[P_n] = \frac{k_p [M][P_{n-1}]}{(k_p + k_{trm}) [M] + (k_{td} + k_{tc}) [P] + \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt}} 
\]  

(1.47)

\[
[P] = \sum_{i=1}^{n} [P_i] = \lambda_0 
\]  

(1.48)

\[
\frac{d[D_2]}{dt} = k_{trm} [M][P_2] + k_{td}[P_2][P] + \frac{1}{2} k_{tc}[P_1]^2 - \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt} [D_2] 
\]  

(1.49)

\[
\vdots 
\]

\[
\frac{d[D_n]}{dt} = k_{trm} [M][P_n] + k_{td}[P_n][P] + \frac{k_{tc}}{2} \sum_{j=1}^{n-1} [P_j][P_{n-j}] - \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt} [D_n] 
\]  

(1.50)

1.2.3 Experimental Description

Materials and Instruments

Free-radical isothermal bulk polymerization reactions were conducted in a 500-mL jacketed round-bottom flask (Lab-Glass, Vineland, NJ, see Figure 1.1). All of the experiments used