Contents

Preface *ix*

1 Introduction *1*
1.1 Special Features of Polymers *1*
1.2 Structures in Polymers and Their Influence on Processing and Application Properties *3*
1.2.1 Chain Length, Molecular Mass, Moments, and Mean Values *3*
1.2.2 Rheological Properties *6*
1.2.3 Constitutional Isomers *7*
1.2.4 Architectural Isomers *9*
1.2.5 Copolymers *11*
1.3 Some Analytical Methods for Model Validation *13*
1.4 Description of Polymer Properties *15*
1.4.1 Chemical Master Equations *17*
1.4.2 Approaches to Polymer Properties *21*
1.4.3 Stochastic and Deterministic Simulation *22*

2 Polymer Reactions *25*
2.1 Module Concept *25*
2.2 Rate Coefficients in Polymerization Reactions *26*
2.3 Building Macromolecules *28*
2.4 Only Chain-Forming Reactions Take Place, Step-Growth Polymerization *30*
2.4.1 Only One Type of End Group: The $A - A$ Case, A Reacting with A *31*
2.4.2 Two Types of Functional Groups A and B at One Molecule; A Reacts with B *40*
2.4.3 Introducing Monofunctional Molecules to Control Degree of Polymerization *41*
2.4.4 Addition of a Second Bifunctional Monomer, Two Functional Groups on Two Different Molecular Species *43*
2.4.5 Reversible Reactions *49*
2.5 Chain-Growth Polymerization – Initiation Required *58*
2.5.1 Living Polymerization – Only Initiation and Propagation (Chain Growth) Take Place *59*

2.5.1.1 Moment Equations *65*
2.5.2 Living Polymerization Together with Chain Depropagation *68*
2.5.3 Initiation and Chain Growth with Transfer Reactions *75*
2.5.4 Initiation and Chain Growth with Deactivation *76*
2.5.5 Initiation and Chain Growth with Chain Termination *77*
2.5.5.1 Termination by Disproportionation *84*
2.5.5.2 Termination by Combination *84*
2.5.5.3 Transfer to Monomer or Transfer Agent *86*
2.5.5.4 Transfer to Polymer *87*
2.5.5.5 Propagation with Change of Characteristics *89*
2.5.5.6 β-Scission *90*
2.6 Copolymerization *91*
2.6.1 Conventional Description of Copolymer Composition *91*
2.6.2 Characteristic Values for the Characterization of Copolymers *94*
2.6.3 Modules for the Description of Copolymerization *97*
2.6.4 Extended Description of a Copolymer *101*
2.6.5 Distributed Counters *104*
2.7 Nonlinear Polymerization *106*
2.7.1 Branching; Graft Polymers via Copolymerization, (Grafting through) *106*
2.7.2 Cross-Linking via Copolymerization *107*
2.7.3 Nonlinear Structures by Polymerization from an Existing Chain, Grafting from *109*
2.7.4 Cross-Linking of Preformed Linear Macromolecules by Low-Molecular-Mass Compounds *111*
2.7.5 Nonlinear Step Growth *111*
2.7.6 Higher Dimensional Models *113*
2.8 List of Modules *114*
2.8.1 Elemental Kinetic *115*
2.8.2 Combination (*P, Q, T, A*) *116*
2.8.3 Statistical Degradation (*P, Q, T, A, B*) *119*
2.8.4 Change of Characteristics (*P, Q, A, B*) *120*
2.8.5 Intermolecular Transfer (*P, Q, T, R, A*) *121*
2.8.6 Cross Transfer (*P, Q, T, R, A*) *123*
2.8.7 Initiation (*P, A, B, C, m*) *124*
2.8.8 Propagation (*P, Q, M, A, m*) *125*
2.8.9 Depropagation (*P, Q, M, A, B, m*) *127*
2.8.10 Transfer (*P, Q, T, M*) *128*
2.8.11 Disproportionation (*P, Q, R, T, A*) *129*
2.8.12 Transfer to Polymer (*P, Q, T, R, A*) *131*
2.8.13 Scission (*P, Q, T, A, B*) *132*
2.8.14 Cross-Linking (*P, Q, T, A*) *133*
2.8.15 Flow (A_1, A_2) *134*
2.8.16 Phase Transfer (A_1, A_2) *135*
2.8.17 Example System *135*

3 Reactors for Polymerization Processes *139*
3.1 Introduction *140*
3.2 Well-Mixed (Ideal) Batch Reactor (BR) *141*
3.2.1 Aspects of the Overall Mass Balance *143*
3.2.2 Heat Balance in a Batch Reactor *144*
3.2.3 Polymer Properties in Batch Reactors *148*
3.3 Semi-Batch Reactor (Semi-BR) *149*
3.4 The Continuous Stirred Tank Reactor (CSTR) *151*
3.4.1 Homogeneous Continuous Stirred Tank Reactor (HCSTR) *151*
3.4.2 Cascade of HCSTR *156*
3.4.3 Segregated Continuous Stirred Tank Reactor (SCSTR) *157*
3.5 Tubular Reactors *158*
3.5.1 Plug Flow Reactor (PFR) *158*
3.5.2 Laminar Tubular Reactor *159*
3.6 Nonideal Reactor Models with Partial Backmixing *159*
3.7 Comparison of Reactors *161*

4 Phases and Phase Transitions *163*
4.1 Treatment of Volumes and Concentrations *164*
4.2 Phase Transfer Modules *165*
4.2.1 Two-Film Theory *166*
4.2.2 Examples for Phase Transfer Steps *169*
4.2.2.1 Evaporation of a Pure Volatile Compound *169*
4.2.2.2 Vapor–Liquid Equilibrium of Volatile Compounds *170*
4.2.2.3 Adsorption of Gaseous Compounds *170*
4.2.2.4 Vapor Pressure Above a Polymer Solution *172*
4.2.2.5 Demixing in Polymer Solutions *174*
4.2.3 Example: Phase Transfer During Polymerization; Living Anionic Polymerization of Butadiene *175*
4.2.4 Summarizing Remarks to the Phase Change Module *178*
4.3 Multiphase Polymerization Systems *179*
4.3.1 Suspension Polymerization *179*
4.3.2 Precipitation/Dispersion Polymerization *180*
4.3.3 Emulsion Polymerization *181*

5 Numerical Methods *193*
5.1 Introduction *193*
5.2 Ordinary Differential Equations *195*
5.2.1 Consistency and Convergence *195*
5.2.2 Stability *197*
5.2.3 Error Control *200*
5.2.4 A Practical Guide to ODE Solvers *205*
5.2.4.1 List of Explicit Methods and Solvers for Non-Stiff ODEs *206*
5.2.4.2 List of Implicit Methods and Solvers for Stiff ODEs and Differential Algebraic Equations (DAEs) *206*
5.3 Countable Systems of Ordinary Differential Equations – CODEs *208*
5.3.1 Theoretical Aspects *208*

5.3.2 The Chain-Length Range *209*
5.3.3 Initialization of Polymer Distributions *211*
5.3.4 Approximation Schemes *212*
5.4 Estimating the Numerical Error *217*
5.5 Monte Carlo Methods *220*
5.6 The Modeling Cycle: Dealing with Different Errors *223*

6 Parameter Estimation *227*
6.1 Introduction: Forward and Inverse Problems *227*
6.2 General Theory *230*
6.2.1 Introduction *230*
6.2.2 The Minimization Problem *232*
6.2.3 Sensitivity Analysis *235*
6.3 Correlated Parameters *236*
6.3.1 Damping *237*
6.3.2 Essential Directions *238*
6.4 Example: Parameter Dependencies and Condition *240*

7 Styrene Butadiene Copolymers *251*
7.1 Model Description *251*
7.2 Components of the Model *251*
7.2.1 Low-Molecular-Weight Compounds *251*
7.2.2 Polymer Distributions *252*
7.2.3 Sequence Distributions *253*
7.2.4 Counters *253*
7.2.5 Computation of Characteristic Values for Copolymers from Counters *254*
7.3 Reaction Modules *254*
7.3.1 Chain Initiation *254*
7.3.2 Chain Propagation *255*
7.3.3 LiH-Elimination *256*
7.3.4 Chain Transfer *256*
7.3.5 Re-Initiation by 1-Phenyl-1-Lithium Ethane *257*
7.3.6 Balance Steps *257*
7.4 Exemplary Simulations *258*
7.5 Exemplification of the Modeling Cycle for the Styrene–Butadiene Example *266*

References *269*

Appendix *277*

Index *283*