CONTENTS

Contributors                                         xiii
Preface                                              xv

1  Fundamentals of Solid State Polymerization          1
   C. D. Papaspyrides and S. N. Vouyiouka

   1.1  Introduction, 2
        1.1.1  Polymers and Plastics, 2
        1.1.2  Polymerization Processes, 3
        1.1.3  Introduction to Solid State Polymerization, 10

   1.2  Solid State Polymerization of Chain-Growth Polymers (Solid
        State Polyaddition), 11

   1.3  Solid State Polymerization of Step-Growth Polymers (Solid
        State Polycondensation), 14
        1.3.1  Monomer Solid State Polymerization (Direct SSP), 16
        1.3.2  Prepolymer Solid State Polymerization (Post-SSP, Solid
                State Finishing), 21

   1.4  Solid State Polymerization Apparatus and Assemblies, 26

   1.5  Solid State Applications in the Polymer Industry, 28
        1.5.1  Solid State Polymerization Advantages, 28
        1.5.2  Post–Solid State Polymerization Application in Polyamides, 28

   1.6  Conclusions, 30
2 Solid State Polymerization Chemistry and Mechanisms: Unequal Reactivity of End Groups
   Haibing Zhang and Saleh A. Jabarin

2.1 Introduction, 40
2.2 Special Characteristics of Solid State Polymerization, 40
2.3 Classical Kinetic Equations in Solid State Polymerization, 41
2.4 Model of Molecular Morphology and Chain-End Movement, 42
   2.4.1 Definition of Chain-End Length in the Amorphous Phase, 42
   2.4.2 How End Groups Move During Solid State Polymerization, 45
   2.4.3 How Chain-End Length Affects the Movement of End Groups, 46
2.5 Reactivity of End Groups, 47
   2.5.1 Principles of Equal Reactivity of End Groups in Melt Polymerization, 47
   2.5.2 Principles of Unequal Reactivity of End Groups in Solid State Polymerization, 47
   2.5.3 Sources of Low Reactivity of End Groups, 48
2.6 Why Intrinsic Viscosity Levels Off During Solid State Polymerization, 50
   2.6.1 Definition of Residual Average Radius and Residual End-Group Concentration, 50
   2.6.2 Relationship Between $\bar{R}_r$ and $\bar{R}$, 51
   2.6.3 Relationship Between $C_r$, $\bar{R}_r$, and Ultimate IV, 52
   2.6.4 Explanation of Temperature Effect on Solid State Polymerization, 54
   2.6.5 Explanation of Initial IV Effect on Solid State Polymerization, 55
2.7 Solid State Polymerization Kinetics, 56
   2.7.1 Kinetic Equation of Ideal Solid State Polymerization, 56
   2.7.2 Empirical Kinetic Equation of Real Solid State Polymerization, 59
2.8 Conclusions, 64

3 Kinetic Aspects of Polyester Solid State Polymerization
   F. Pilati and M. Toselli

3.1 Introduction, 68
3.2 Phenomena Involved in Solid State Polymerization of Polyesters, 69
   3.2.1 Possible Reactions in Solid State Polymerization of Polyesters, 69
3.2.2 Chain Mobility and Diffusion of Low-Molecular-Weight By-Products, 76
3.2.3 Kinetic and Diffusion Equations, 81

3.3 Modeling Solid State Polymerization of Polyesters, 89
3.3.1 Effects of Variables and Predictions Based on Kinetic Models, 98

3.4 Solid State Polymerization of Typical Polyesters, 105
3.4.1 Poly(ethylene terephthalate), 106
3.4.2 Poly(butylene terephthalate), 107
3.4.3 Poly(ethylene naphthalate), 109
3.4.4 Poly(trimethylene terephthalate), 110
3.4.5 Poly(l-lactic acid), 112

3.5 Conclusions, 113

4 Kinetic Aspects of Polyamide Solid State Polymerization 123
S. N. Vouyiouka and C. D. Papaspyrides

4.1 Introduction, 123

4.2 Simple Kinetic Models of Solid State Polyamidation, 128
4.2.1 Fundamental Chemistry in Solid State Polyamidation, 128
4.2.2 Direct Solid State Polyamidation, 130
4.2.3 Prepolymer Solid State Polyamidation, 132

4.3 Simulation of Solid State Polyamidation, 136

4.4 Simple SSP Kinetics: The Case of Poly(hexamethylene adipamide), 139
4.4.1 Solid State Polymerization of Hexamethylenediammonium Adipate, 139
4.4.2 Solid State Polymerization of Poly(hexamethylene adipamide), 143
4.4.3 Compositional Effects in Solid State Polymerization of Poly(hexamethylene adipamide), 148

4.5 Conclusions, 153

5 Catalysis in Solid State Polymerization Processes 159
Rudolf Pfaendner

5.1 Introduction, 159

5.2 Catalysts in Polyester Solid State Polymerization Processes, 161
5.2.1 Metal-Type Catalysts, 161
5.2.2 Phosphorus- and Sulfur-Based Catalysts, 164

5.3 Catalysts in Polyamide Solid State Polymerization Processes, 167
5.4 Reactive Additives in Solid State Polymerization Processes, 170
5.5 Inert Additives in Solid State Polymerization Processes, 173
5.6 Conclusions, 173

6 High-Pressure Solid State Polymerization of Polyamide Monomer Crystals

Tokimitsu Ikawa

6.1 Introduction, 179
6.2 High-Pressure Solid State Polymerization, 182
6.2.1 Crystals and Characteristics of Monomers, 182
6.2.2 HP-SSP Method for Polyamide Monomer Crystals, 183
6.3 Polymerizability and Structure Formation, 184
6.3.1 Polymerizability and Structure Formation of $\omega$-Amino Acid Crystals to Polyamide Crystals, 184
6.3.2 Polymerizability of Polyamide Salt Crystals to Polyamide Crystals, 187
6.3.3 Structure Formation of Polyamide Salt Crystals to Polyamide Crystals, 191
6.4 Conclusions, 195
6.4.1 Polymerizability, 195
6.4.2 Structure Formation, 195


Kevin C. Seavey and Y. A. Liu

7.1 Introduction, 200
7.2 Solid State Polymerization Modeling Guide, 200
7.3 Fundamentals of Solid State Polymerization Reactors, 203
7.3.1 Material and Energy Balances, 203
7.3.2 Mass and Heat Transfer, 206
7.3.3 Reaction Kinetics, 209
7.3.4 Physical Properties, 217
7.4 Numerical Solution, 222
7.5 Example Simulation and Application, 225
7.6 Modifications to Account for Crystallization, 227
7.7 Conclusions, 229