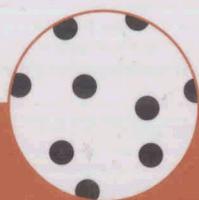


Principles and Applications of  
**EMULSION  
POLYMERIZATION**



CHORNG-SHYAN CHERN

 WILEY

# CONTENTS

<b>Preface</b>	<b>xi</b>
<b>1 Introduction</b>	<b>1</b>
1.1 Free Radical Polymerization / 1	
1.1.1 Free Radical Polymerization Mechanisms / 1	
1.1.2 Free Radical Polymerization Kinetics / 3	
1.2 Emulsion Polymerization / 5	
1.2.1 Conventional Emulsion Polymerization / 5	
1.2.2 Emulsion Polymerization Processes / 6	
1.2.3 Miniemulsion Polymerization / 8	
1.2.4 Microemulsion Polymerization / 9	
1.2.5 Inverse Emulsion Polymerization / 10	
1.3 Colloidal Stability / 11	
1.3.1 A Critical but Often Ignored Issue / 11	
1.3.2 Electrostatic Interactions / 12	
1.3.3 Steric Interactions / 13	
1.3.4 Mechanical Stability / 14	
1.4 Some Performance Properties for Industrial Applications / 15	
1.4.1 Rheology / 15	
1.4.2 Film Formation / 16	
References / 19	
<b>2 Interfacial Phenomena</b>	<b>23</b>
2.1 Thermodynamic Consideration / 23	
2.1.1 Emulsification of Oil in Water / 23	
2.1.2 Interfaces / 25	
2.1.3 Surfactant Molecules Adsorbed at an Interface / 26	

2.2	Surfactants / 26
2.2.1	Critical Micelle Concentration (CMC) / 27
2.2.2	Hydrophile–Lipophile Balance (HLB) / 27
2.2.3	Solubility Parameter / 29
2.3	Colloidal Stability / 32
2.3.1	Van der Waals Forces / 32
2.3.2	Electrostatic Interactions / 36
2.3.3	Steric Interactions / 44
2.3.4	Kinetics of Flocculation / 48
	References / 50

### **3 Particle Nucleation Mechanisms**

**53**

3.1	Micellar Nucleation / 54
3.1.1	Harkins–Smith–Ewart Theory / 54
3.1.2	Competitive Absorption of Free Radicals by Micelles and Particle Nuclei / 57
3.2	Homogeneous Nucleation / 60
3.2.1	Formation of Particle Nuclei in the Continuous Aqueous Phase / 60
3.2.2	Hansen–Ugelstad–Fitch–Tsai (HUFT) Model / 63
3.3	Coagulative Nucleation / 65
3.3.1	General Features of Coagulative Nucleation / 65
3.3.2	Coagulative Nucleation Model Development / 66
3.4	Mixed Mode of Particle Nucleation Mechanisms / 68
3.5	Surfactant-Free Emulsion Polymerization / 71
3.6	Experimental Work on Particle Nucleation / 76
3.6.1	A Dilemma about Particle Nucleation Mechanisms / 76
3.6.2	Some Representative Experimental Data of Particle Nucleation / 77
3.6.3	Some Potential Techniques for Studying Particle Nucleation / 82
3.6.4	Effects of Surfactant Concentration on Particle Nucleation / 86
3.7	Nonionic and Mixed Surfactant Systems / 87
3.7.1	Nonionic Surfactant Systems / 88
3.7.2	Mixed Anionic and Nonionic Surfactant Systems / 89
	References / 91

## **4 Emulsion Polymerization Kinetics**

**95**

- 4.1 Emulsion Polymerization Kinetics / 96
  - 4.1.1 Smith–Ewart Theory / 96
  - 4.1.2 Pioneering Kinetic Models for Predicting Average Number of Free Radicals per Particle / 100
- 4.2 Absorption of Free Radicals by Latex Particles / 103
  - 4.2.1 Collision- and Diffusion-Controlled Models / 104
  - 4.2.2 Propagation-Controlled Model / 106
  - 4.2.3 Some Controversial Issues / 108
- 4.3 Desorption of Free Radicals Out of Latex Particles / 109
  - 4.3.1 Desorption of Free Radicals in Emulsion Homopolymerization Systems / 110
  - 4.3.2 Desorption of Free Radicals in Emulsion Copolymerization Systems / 112
  - 4.3.3 Effect of Interfacial Properties on Desorption of Free Radicals / 113
- 4.4 Growth of Latex Particles / 114
  - 4.4.1 Thermodynamic Consideration / 114
  - 4.4.2 Concentrations of Comonomers in Emulsion Copolymerization Systems / 116
  - 4.4.3 Competitive Growth of Latex Particles / 119
- 4.5 Polymer Molecular Weight / 120
- References / 123

## **5 Miniemulsion Polymerization**

**128**

- 5.1 Polymerization in Monomer Droplets / 129
- 5.2 Stability of Monomer Emulsions / 130
  - 5.2.1 Ostwald Ripening Effect / 130
  - 5.2.2 Role of Costabilizer in Stabilizing Monomer Emulsions / 132
- 5.3 Type of Costabilizers in Miniemulsion Polymerization / 133
- 5.4 Miniemulsion Polymerization Mechanisms and Kinetics / 135
  - 5.4.1 Initial Conditions for Miniemulsion Polymerization Systems / 135
  - 5.4.2 Particle Nucleation Mechanisms / 136
  - 5.4.3 Effect of Functional Monomers and Initiators on Particle Nucleation / 140
  - 5.4.4 Polymerization Kinetics / 142

- 5.5 Versatility of Miniemulsion Polymerization / 145
  - 5.5.1 Catalytic Chain Transfer Reaction / 147
  - 5.5.2 Living Free Radical Polymerization / 147
  - 5.5.3 Step Polymerization / 148

References / 150

## **6 Microemulsion Polymerization**

**154**

- 6.1 Introduction / 154
- 6.2 Formation and Microstructure of Microemulsions / 155
  - 6.2.1 Formation of Microemulsions / 155
  - 6.2.2 Factors that Govern Microemulsion Structures / 157
- 6.3 O/W Microemulsion Polymerization / 158
  - 6.3.1 General Features / 158
  - 6.3.2 Polymerization Mechanisms and Kinetics / 159
- 6.4 W/O Microemulsion Polymerization / 167
- 6.5 Polymerization in Continuous or Bicontinuous Phases of Microemulsions / 169

References / 170

## **7 Semibatch and Continuous Emulsion Polymerizations**

**175**

- 7.1 Semibatch Emulsion Polymerization / 175
  - 7.1.1 Pseudo-Steady-State Polymerization Behavior / 175
  - 7.1.2 Polymerization Mechanisms and Kinetics / 177
  - 7.1.3 Mathematical Modeling Studies / 186
- 7.2 Continuous Emulsion Polymerization / 187
  - 7.2.1 General Features of Continuous Emulsion Polymerization Processes / 187
  - 7.2.2 Particle Nucleation and Growth Mechanisms / 191
- 7.3 Development of Commercial Continuous Emulsion Polymerization Processes / 194

References / 196

## **8 Emulsion Polymerizations in Nonuniform Latex Particles**

**200**

- 8.1 Origin of Nonuniform Latex Particles / 200
- 8.2 Seeded Emulsion Polymerizations / 201

8.3	Factors Affecting Particle Morphology / 202	
8.3.1	Effect of Initiators / 202	
8.3.2	Effect of Monomer Addition Methods / 203	
8.3.3	Effect of Polymer Molecular Weight / 204	
8.3.4	Effect of Volume Fractions of Polymer Pairs / 205	
8.3.5	Effect of Polymerization Temperature / 205	
8.4	Morphology Development in Latex Particles / 205	
8.4.1	Thermodynamic Considerations / 205	
8.4.2	Nonequilibrium Morphology Development / 206	
8.4.3	Techniques for Characterization of Particle Morphology / 210	
8.5	Polymerization Kinetics in Nonuniform Latex Particles / 211	
8.5.1	Pioneering Studies / 212	
8.5.2	Effect of Distribution of Free Radicals in Nonuniform Latex Particles / 213	
	References / 220	

## **9 Applications of Emulsion Polymers**

**223**

9.1	Physical Properties of Emulsion Polymers / 224
9.1.1	Effect of Polymer Molecular Weight / 224
9.1.2	Effect of Polymer Morphology / 225
9.1.3	Effect of Crosslinking Reactions / 229
9.2	Rheological Properties of Emulsion Polymers / 230
9.3	Film Formation of Emulsion Polymers / 233
9.4	Foaming and Antifoaming Agents / 236
9.5	Wetting / 238
9.6	Surface Modifications / 241
9.7	Stability of Latex Products / 242
	References / 245