Hyperbranched Polymers
Synthesis, Properties, and Applications

Edited by
Deyue Yan, Chao Gao, and Holger Frey

WILEY
A John Wiley & Sons, Inc., Publication
# Contents

**Preface** xiii  
**Contributors** xv  

1. Promising Dendritic Materials: An Introduction to Hyperbranched Polymers  
   1.1 Importance of Branching  
   1.2 Polymer Architecture  
   1.3 Dendritic Polymers  
   1.4 Hyperbranched Polymers  
      1.4.1 Concept and History  
      1.4.2 Structure and Properties  
      1.4.3 Synthesis Philosophy  
      1.4.4 Applications  
   1.5 Conclusions  
   1.6 References  

2. Polycondensation of AB<sub>x</sub> Monomers  
   2.1 Introduction  
   2.2 Statistical Consideration  
      2.2.1 Polymerization Behavior  
      2.2.2 Degree of Branching  
   2.3 Polymerization of AB<sub>x</sub>-Type Monomers  
      2.3.1 C–C Coupling Reactions  
      2.3.1.1 Metal-Catalyzed Cross Couplings  
      2.3.1.2 Diels–Alder Reactions  
      2.3.1.3 Nucleophilic Substitution by Activated Methylenes  
      2.3.1.4 Electrophilic Acylations  
      2.3.2 C–O Coupling Reactions  
      2.3.2.1 Nucleophilic Substitution Reactions by Phenoxides or Alkoxides
## 2.3.2.2 Esterification of Carboxylic Acid Derivatives 46
## 2.3.2.3 Ring-Opening Reaction of Epoxides 54

### 2.3.3 C–N Coupling Reactions 55

- **2.3.3.1 Condensation of Amines and Carboxylic Acid Derivatives** 55
- **2.3.3.2 Nucleophilic Addition of Amines** 59
- **2.3.3.3 Other C–N Coupling Reactions** 62

### 2.3.4 Si–C or Si–O Coupling Reactions 62

- **2.3.4.1 Hydrosilylation Reactions** 62
- **2.3.4.2 Condensation Reactions** 68
- **2.3.4.3 Other Si-Containing Reactions** 69

### 2.3.5 Other Coupling Reactions 70

- **2.3.5.1 C–O or C–N Coupling Reactions of Isocyanates** 70
- **2.3.5.2 C–S Coupling Reactions** 72

## 2.4 References 74


### 3.1 Introduction 79
### 3.2 Theoretical Treatment of $A_2 + B_3$ Polymerization 81
### 3.3 Polymerization of Symmetrical Monomer Pairs 84

- **3.3.1 Polycondensation of $A_2$ and $B_3$ Monomers** 84
  - **3.3.1.1 Polyamides** 84
  - **3.3.1.2 Polymides** 87
  - **3.3.1.3 Polyethers** 89
  - **3.3.1.4 Polysters** 93
  - **3.3.1.5 Polycarbonates** 97
  - **3.3.1.6 Polyurethanes** 97

- **3.3.2 Proton-Transfer Polymerization of $A_2$ and $B_3$ Monomers** 99
- **3.3.3 The Michael Addition Polymerization of $A_2$ and $B_3$ Monomers** 100

### 3.4 Conclusions 104
### 3.5 References 105

## 4. Synthesis of Hyperbranched Polymers via Polymerization of Asymmetric Monomer Pairs 107

### 4.1 Introduction 107
### 4.2 General Description of Polymerization of Asymmetric Monomer Pairs 108
4.3 Hyperbranched Polymers Prepared by Polymerization of Asymmetric Monomer Pairs 110

4.3.1 Poly(Sulfoneamine) 110
4.3.2 Poly(Ester Amine) 113
4.3.3 Poly(Amidoamine) 115
4.3.4 Multihydroxyl Hyperbranched Poly(Amine Ester)s 118
4.3.5 Poly(Ester Amide)s 120
4.3.6 Polyesters 123
4.3.7 Poly(Urea-Urethane)s 127
4.3.8 Other Polymers 129
4.3.9 Highly Branched Copolymers 131

4.4 Conclusions 133
4.5 References 136

5. Self-Condensing Vinyl Polymerization 139

5.1 Introduction 139
5.2 Self-Condensing Vinyl Polymerization 140

5.2.1 General Principles 140
5.2.2 Various Mechanisms of SCVP 144
5.2.3 Kinetics and MWD 145
5.2.4 Degree of Branching 148
5.2.5 Comparison with Experimental Data 150

5.3 Self-Condensing Vinyl Copolymerization (SCVCP) 150

5.3.1 Experimental Data 151
5.3.2 Kinetics and MWD 153
5.3.3 Degree of Branching 159
5.3.4 Comparison with Experimental Data 161

5.4 Self-Condensing Processes in Presence of Initiators 162

5.4.1 Kinetics and MWD 162
5.4.1.1 Batch Reactions 162
5.4.1.2 Semibatch Polymerization (Slow Initiator Addition) 164

5.4.2 Degree of Branching 165
5.4.2.1 Batch Polymerization 165
5.4.2.2 Semibatch Polymerization 166

5.4.3 Comparison with Experimental Data 167

5.5 SCVP of Macroinimers 167
5.6 Surface-Grafted Hyperbranched Polymers 169
5.7 References 172

6. Ring-Opening Multibranching Polymerization 175

6.1 Introduction 175
### 6.2 Classification of Ring-Opening Multibranching Polymerizations

- 6.2.1 Cationic Ring-Opening Multibranching Polymerizations 178
- 6.2.2 Anionic Ring-Opening Multibranching Polymerizations 183
- 6.2.3 Catalytic Ring-Opening Multibranching Polymerizations 189

### 6.3 Core-Containing Hyperbranched Polymers By Ring-Opening Multibranching Polymerization 195

### 6.4 Conclusion and Perspectives 198

### 6.5 References 200

### 7. Hyperbranched Copolymers Synthesized by Cocondensation and Radical Copolymerization 203

- 7.1 Introduction 203
- 7.2 Cocondensation of ABₙ and a Comonomer 204
  - 7.2.1 ABₙ + AB Approach 204
  - 7.2.2 AB₂ + AB₂ Approach 211
  - 7.2.3 Combined ROP/AB₂ Approach 212
- 7.3 Cocondensation of A₂ + B₂ + BB₂ (or B'B₂) 214
- 7.4 SCVCP Via Charge-Transfer Complex Inimer 215
- 7.5 Free Radical Copolymerization of Multifunctional Vinyl Monomers 218
- 7.6 Conclusion 221
- 7.7 References 223

### 8. Convergent Synthesis of Hyperbranched Polymers and Related Approaches 227

- 8.1 Introduction 227
- 8.2 Convergent Control in Hyperbranched Synthesis 228
- 8.3 Results 231
  - 8.3.1 Hyperbranched Polymers by Convergent Living Anionic Polymerization 231
    - 8.3.1.1 Hyperbranched Polymers from CDMSS and Polystyrene (PS) 232
    - 8.3.1.2 Copolymerization of CDMSS and Styrene 236
    - 8.3.1.3 Hyperbranched Polymer from VBC and PS 237
    - 8.3.1.4 Characterization of Hyperbranched PS 238
    - 8.3.1.5 Hyperbranched Polyisoprene 239
    - 8.3.1.6 Convergent Hyperbranching with 4-Vinylstyrene Oxide 240
  - 8.3.2 Complex Branching by Convergent Hyperbranched Polymerization 241
10.5 Hyperbranched Poly(Aryleneethynylenes) 289
10.6 Conclusion 295
10.7 References 297

11. Degree of Branching (DB) 301

11.1 Definition of the Degree of Branching (DB) 301
  11.1.1 Single Highly Branched Molecules 302
  11.1.2 A System of Hyperbranched Molecules 304

11.2 Determination of DB 305
  11.2.1 Direct Determination 305
  11.2.2 Indirect Methods 307

11.3 The Value Range of DB 308

A11.4 Appendix 311
  A11.4.1 Numbers of Isomers in Hyperbranched Polymers 311
  A11.4.2 Number of Units of Different Substitution Degree in Random
    Polymerization of AB_j Monomer 313

11.5 References 314

12. Influence of Branching Architecture on Polymer Properties 317

12.1 Introduction 317
12.2 Influence of Branching Architecture on Polymer Properties 318
  12.2.1 Rheological Property 318
  12.2.2 Crystallization and Melting Behaviors 320
  12.2.3 Glass Transition 321
  12.2.4 Thermal and Hydrolytic Degradations 323
  12.2.5 Phase Characteristics 324
  12.2.6 Optoelectronic Properties 324
  12.2.7 Encapsulation Capability 325
  12.2.8 Self-Assembly Behavior 325
  12.2.9 Biomedical Applications 327

12.3 Conclusions 329
12.4 References 329

13. Kinetic Theory of Hyperbranched Polymerization 333

13.1 Introduction 333
13.2 AB_2-Type Polycondensation 335
  13.2.1 Molecular Size Distribution Function 336
  13.2.2 Average Degree of Polymerization and Polydispersity 339
  13.2.3 Substitution Effect 340
Contents xi

13.2.4 Degree of Branching 343
13.2.5 Effect of Core Molecules 346

13.3 Copolycondensation of AB2- and AB-Type Monomers 351
13.3.1 Molecular Size Distribution Function 351
13.3.2 Degree of Branching 353

13.4 Self-Condensing Vinyl Polymerization 354
13.4.1 Distribution Function and Molecular Parameters 357
13.4.2 Degree of Branching 359
13.4.3 Effect of Core Initiators 362

13.5 References 366

14. Grafting and Surface Properties of Hyperbranched Polymers 369

14.1 Introduction 369
14.2 Surface Grafting 370
14.2.1 “Grafting from” Approach 371
14.2.1.1 Step-by-Step Methodology 371
14.2.1.2 Graft-on-Graft Technique 373
14.2.1.3 Radical Polymerization 375
14.2.1.4 Ring-Opening Polymerization 377
14.2.2 “Grafting to” Approach 378

14.3 Surface Properties of Hyperbranched Polymers 380
14.4 Conclusions 382
14.5 References 383

15. Biological and Medical Applications of Hyperbranched Polymers 387

15.1 Introduction 387
15.2 Gene Delivery 388
15.2.1 Linear and Hyperbranched Poly(ethyleneimine) as Nonviral Gene Vectors 388
15.2.2 Modification of Poly(ethyleneimine) and Use of Adjuvant Polyglycerol 390
15.2.3 Hyperbranched Alternatives for Poly(ethyleneimine) as Gene Vectors 393

15.3 Drug Delivery 397
15.3.1 Drug Encapsulation and Conjugation 397
15.3.2 Controlled Release of Pesticides 401

15.4 Biomaterials 401
15.4.1 Surface Modification 402
### 16. Applications of Hyperbranched Polymers in Coatings, as Additives, and in Nanotechnology

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.1 Introduction</td>
<td>415</td>
</tr>
<tr>
<td>16.2 Hyperbranched Polymers in Coating and Resin Applications</td>
<td>416</td>
</tr>
<tr>
<td>16.2.1 Hyperbranched Polyesters in Reactive Formulation Application</td>
<td>417</td>
</tr>
<tr>
<td>16.2.2 Hyperbranched Poly(esteramide)s</td>
<td>421</td>
</tr>
<tr>
<td>16.2.3 Hyperbranched Poly(urea-urethane)s</td>
<td>421</td>
</tr>
<tr>
<td>16.3 Hyperbranched Polymers as Additives</td>
<td>423</td>
</tr>
<tr>
<td>16.3.1 Additives for Linear Thermoplastics</td>
<td>423</td>
</tr>
<tr>
<td>16.3.2 Printing Systems</td>
<td>425</td>
</tr>
<tr>
<td>16.3.3 Stabilizers</td>
<td>425</td>
</tr>
<tr>
<td>16.4 Applications of Hyperbranched Polymers in Nanotechnology</td>
<td>426</td>
</tr>
<tr>
<td>16.4.1 Nanocomposites and Nanohybrids</td>
<td>426</td>
</tr>
<tr>
<td>16.4.2 Nanoporous Materials</td>
<td>430</td>
</tr>
<tr>
<td>16.5 Applications in Thin Films and Sensorics</td>
<td>431</td>
</tr>
<tr>
<td>16.6 References</td>
<td>434</td>
</tr>
</tbody>
</table>

### 17. Conclusions and Perspective: Toward Hyperbranched/Dendritic States

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.1 Achievements and Problems</td>
<td>441</td>
</tr>
<tr>
<td>17.1.1 Ten Main Achievements</td>
<td>441</td>
</tr>
<tr>
<td>17.1.2 Ten Noteworthy Problems and Topics</td>
<td>448</td>
</tr>
<tr>
<td>17.2 Role of Hyperbranched Polymers in the Twenty-First Century</td>
<td>449</td>
</tr>
<tr>
<td>17.3 Hyperbranched/Dendritic State</td>
<td>451</td>
</tr>
<tr>
<td>17.4 References</td>
<td>452</td>
</tr>
</tbody>
</table>

Index 453