

Plastics from Microbes

Microbial Synthesis of Polymers and Polymer Precursors

Edited by David P. Mobley

With 93 Figures, 4 in Full Color



Hanser Publishers, Munich Vienna New York

Hanser/Gardner Publications, Inc., Cincinnati

Contents

Contributors	xv
1 Introduction to Microbial Synthesis of Polymers and Polymer Precursors	1
<i>David P. Mobley</i>	
References	4
2 Polyhydroxyalkanoates	5
<i>David Byrom</i>	
2.1 Introduction	5
2.2 Physiology and Biochemistry of Synthesis	7
2.2.1 PHB Synthesis	7
2.2.2 Granule Structure	9
2.2.3 Synthesis in <i>Azotobacter</i>	9
2.2.4 PHB/HV Copolymer Synthesis	10
2.2.5 PHB/HB Synthesis from Unrelated Substrates	11
2.2.6 PHA Synthesis by <i>Pseudomonas</i> Species	13
2.2.6.1 PHA Synthesis from Related Substrates	13
2.2.6.2 PHA Synthesis from Unrelated Substrates	14
2.2.7 PHA Containing Nonnatural Monomers	15
2.3 Molecular Biology of PHA Synthesis	16
2.3.1 Molecular Biology of PHB Synthesis	17
2.3.2 Genetics of PHA Synthesis in <i>Pseudomonas</i>	19
2.3.3 Molecular Biology of PHA Synthesis in Other Organisms	20
2.3.4 PHA Synthesis in Plants	21
2.4 Fermentation	22
2.5 Industrial Significance of PHA	22
2.6 Commercial Production of PHA	23
2.7 Polymer Properties	25
2.7.1 Biodegradation of PHB/HV	26
2.7.2 PHA Degradation	28
2.8 Chemical Synthesis of PHB	28
2.8.1 Chemical Routes	29

2.9	Other Biodegradable Polymers	29
2.9.1	Starch-based Materials	30
2.9.2	Polylactic Acid	30
2.9.3	Condensation Polymers	30
	References	31
3	Microbial Production of Structural Protein Polymers	35
	<i>Joseph Cappello and Franco Ferrari</i>	
3.1	Introduction	35
3.1.1	Proteins Differ from Other Polymers	35
3.1.2	Capitalizing on the Potential Utility of Proteins	36
3.1.3	Protein Polymer Production Technology	37
3.2	Protein Structure, Function, and Design	38
3.2.1	Structural Components of Natural Proteins	39
3.2.1.1	Beta Strands	41
3.2.1.2	Alpha Helices	43
3.2.1.3	Reverse Turns	44
3.2.1.4	Collagen Triple Helix	45
3.2.2	Functional Components of Natural Proteins	46
3.2.2.1	Engineering Improved Function	47
3.2.2.2	Novel Functions Built on Common Structures	48
3.2.2.3	Using Nature's Strategies to Engineer Protein Function ..	50
3.2.3	Properties of Natural Structural Proteins	50
3.2.3.1	Silks	51
3.2.3.2	Keratins	52
3.3	Microbial Production of Synthetically Designed Protein Polymers	55
3.3.1	Efficient Production Requires a Biological Approach	55
3.3.1.1	Programming Microorganisms to Produce Foreign Products	56
3.3.1.2	Problems with Biological Production of Foreign Products	59
3.3.2	Expression of Protein Polymers	60
3.3.2.1	Polymer Gene Design and Stability	60
3.3.2.2	Factors Influencing Microbial Production	61
3.3.2.3	Polymer Purification	63
3.3.2.4	Compositional and Molecular Analysis	65
3.3.3	Elements of Protein Polymer Technology	65
3.3.3.1	Polymer Gene Construction	66
3.3.4	Future Goals for Large-scale Manufacturing	70
3.4	Properties of Protein Polymers	71
3.4.1	Bulk Properties	73

3.4.1.1	Crystalline Silklike Protein Polymers	73
3.4.2	Fiber Spinning of Structural Protein Polymers	76
3.5	Protein Polymer Products	81
3.5.1	ProNectin® F: A Biofunctional Protein Polymer	81
3.5.2	Future Biomedical Applications	87
3.6	Summary	88
	References	89
4	Polymers of Lactic Acids	93
	<i>Gregory B. Kharas, Fernando Sanchez-Riera, and David K. Severson</i>	
4.1	Introduction	93
4.2	Monomer Synthesis and Purification	94
4.2.1	Biochemistry and Microbiology	94
4.2.1.1	Background	94
4.2.1.2	Lactic Acid Pathway	94
4.2.1.3	Selection of Organisms	96
4.2.1.3.1	Stereospecificity of the Isomers	96
4.2.1.3.2	Carbohydrate Utilization	97
4.2.1.3.3	Complex Nutrient Requirements	98
4.2.1.4	Metabolic Regulation	99
4.2.1.5	Strain Improvement	101
4.2.1.5.1	Classical Mutagenesis	101
4.2.1.5.2	Genetic Engineering	102
4.2.2	Fermentation Processes	103
4.2.2.1	Environmental Parameters	103
4.2.2.1.1	Effect of pH	103
4.2.2.1.2	Effect of Temperature	103
4.2.2.1.3	Effect of Oxygen	104
4.2.2.1.4	Effect of Agitation	104
4.2.2.2	Basis for Process Design	104
4.2.2.3	Process Configurations	105
4.2.2.3.1	Batch Process	105
4.2.2.3.2	Continuous Process in Continuous Stirred Tank Reactors	106
4.2.2.3.3	Cell Recycle Reactors	107
4.2.2.3.4	Immobilized Cell Reactors	108
4.2.2.3.5	Extractive Fermentation	109
4.2.3	Monomer Recovery and Purification and Properties	110
4.2.3.1	Recovery and Purification of Lactic Acid	110
4.2.3.2	Lactoyllactic Acid and Lactide Processes	112

4.2.3.3	Properties of Lactides	113
4.2.3.4	Process Design	114
4.2.3.5	Lactide Purification	115
4.3	Polymerization of Lactic Acid-Based Monomers	116
4.3.1	Condensation Polymerization of Lactic Acid	116
4.3.2	Ring-Opening Polymerization of Lactide Monomers	116
4.3.2.1	Catalysis and Polymerization Mechanism	116
4.3.2.2	Racemization	117
4.3.2.3	Process Design	118
4.3.2.4	Microstructure	118
4.3.2.5	Copolymerization	119
4.4	Polymer Properties	121
4.4.1	Physical Properties	121
4.4.2	Structure	122
4.4.3	Mechanical Properties	122
4.4.4	Thermal Properties	123
4.4.5	Degradation	124
4.4.6	Applications	125
4.4.6.1	Wound Closure	125
4.4.6.2	Prosthetic Implants	126
4.4.6.3	Controlled Release	127
4.4.6.3.1	Medical Devices	127
4.4.6.3.2	Agricultural Applications	128
4.4.6.4	Other Applications	128
4.5	Economic Aspects of Polymers of Lactic Acid	128
References		130
5	Polyphenylenes from Biosynthetic <i>cis</i>-Dihydroxycyclohexadiene	139
	<i>Dennis G. H. Ballard, A. John Blacker, John M. Woodley, and Stephen C. Taylor</i>	
5.1	Introduction	139
5.2	Synthetic Options for Polyphenylene	140
5.3	Biology of Aromatic Oxidation	141
5.3.1	The Aromatic Pathway	141
5.3.2	Microorganism Selection and Strain Development	143
5.3.3	Biotransformation Options	144
5.4	Bioprocessing: Synthesis of <i>cis</i> -DHCD	147
5.4.1	Biocatalyst Production	147
5.4.2	Biotransformation	148
5.4.2.1	Reactor Selection	148

5.4.2.2	Supply of Aromatic Reactant	148
5.4.2.3	Biocatalyst Kinetics	149
5.4.2.4	Control and Productivity	151
5.4.3	Recovery of <i>cis</i> -DHCD	151
5.5	Polymerization: Synthesis of Polyphenylene	152
5.5.1	Derivatives of <i>cis</i> -DHCD	152
5.5.2	Polymerization of <i>cis</i> -DHCD Derivatives Using Radical Initiators	153
5.5.3	Thermal Conversion to Polyphenylene	158
5.6	Solid State Properties and Applications of Polyphenylene	161
5.7	Future Developments	166
5.8	References	166

6 Biological Production of Hydroxylated Aromatic Hydrocarbons for Aerospace Applications 169

Alan D. Grund, Frederick L. Hedberg, and Loon-Seng Tan

6.1	Introduction	169
6.2	Biological Formation of Specialty Hydroxylated Monomers	171
6.2.1	Biological Hydroxylation of Aromatic Hydrocarbons	171
6.2.2	Possible Biological Routes to Hydroxylated Monomers	173
6.2.3	Isolation and Characterization of Aromatic Hydrocarbon Degraders ..	173
6.2.4	Microbial Metabolism of PA	175
6.2.5	Regulation of PA Pathway	177
6.2.6	Formation and Dehydration of PA Dihydrodiol	177
6.2.7	Strain Improvement	178
6.2.8	Metabolism of BCB	184
6.2.9	Formation and Dehydration of Dihydrodiols	187
6.2.10	Process Development for PA Dihydrodiol Production	189
6.3	Properties and Potential Applications of Acetylene-Terminated Resins	193
6.3.1	Polymerization Chemistry	194
6.3.2	Background of Molecular Structures	195
6.3.3	MHPA Synthesis and Use for Resins	196
6.3.4	Current Synthesis of ATS and Economic Considerations	199
6.4	BCB-Based Polymers	201
6.4.1	Raw Materials for BCB-Based Polymers	202
6.4.2	BCB-Based Polymeric Materials Developed at U.S. Air Force Materials Laboratory	205
6.5	Current and Future Applications of Biotransformations to Aerospace Resins ..	211
6.6	Acknowledgments	213
	References	213

7	Aromatic Hydroxylation by <i>Aspergillus</i> to Make Polymer Precursors	219
	<i>David P. Mobley, Joseph J. Salvo, Susan A. Nye, Jay Spivack, and Kenneth R. Liberty</i>	
7.1	Introduction	219
7.2	Biology	220
7.2.1	Microbiology and Biochemistry	220
7.2.1.1	Background	220
7.2.1.2	Nature and Substrate Specificity of the Hydroxylase	221
7.2.1.3	Enzyme Induction and Biphenyl Hydroxylase Assay	223
7.2.1.4	Further Metabolism of Hydroxylated Products	224
7.2.1.5	Substrate Toxicity	226
7.2.1.6	Aflatoxins	226
7.2.2	Genetics and Molecular Biology	227
7.3	Biotransformation Process	229
7.3.1	Process Conditions	229
7.3.2	Substrate Bioavailability	234
7.3.3	Optimized Bioconversion Conditions	235
7.3.4	Product Recovery	235
7.4	Polymers	237
7.4.1	Polysulfones	237
7.4.2	Polyarylates	238
7.4.3	Polycarbonates	242
7.4.4	Other Polymers	245
7.5	Chemical Synthesis of Alternative Bisphenols	245
7.5.1	4,4'-Dihydroxybiphenyl	245
7.5.2	4,4''-Dihydroxy- <i>m</i> -terphenyl	246
7.6	Status and Future Outlook	247
	References	249
8	Summary and Conclusions	253
	<i>David P. Mobley</i>	
8.1	Summary	253
8.2	Conclusion	257
	References	258
	Index	259