## **CONTENTS**

FO	EFACI REWC			xiii xvii xix
1	An Overview of Polymer-Immobilized Chiral Catalysts and Synthetic Chiral Polymers  Shinichi Itsuno			
	1.1	Introduc	etion / 1	
	1.2		ric Chiral Catalyst / 2	
		1.2.1	Polymers Having a Chiral Pendant Group / 4	
		1.2.2	Main-chain Chiral Polymers / 4	
		1.2.3	Dendrimer-supported Chiral Catalysts / 6	
		1.2.4	Helical Polymers / 6	
		1.2.5	Multicomponent Asymmetric Catalysts / 7	
		1.2.6	Continuous Flow System / 8	
	1.3	Synthes	is of Optically Active Polymers / 8	
		1.3.1	Asymmetric Reaction on Polymer / 9	
		1.3.2	Helical Polymers and Hyperbranched Polymers / 9	
		1.3.3	Heteroatom Chiral Polymers / 10	
		1.3.4	Asymmetric Polymerization / 11	
	Refer	ences / 1	11	

2	•	mer-Immobilized Chiral Organocatalyst	17
		Haraguchi and Shinichi Itsuno	
	2.1	Introduction / 17	
	2.2	Synthesis of Polymer-immobilized Chiral Organocatalyst / 18	
	2.3	Polymer-immobilized Cinchona Alkaloids / 22	
	2.4	Other Polymer-immobilized Chiral Basic Organocatalysts / 27	
	2.5	Polymer-immobilized Cinchona Alkaloid Quaternary Ammonium Salts / 28	
	2.6	Polymer-immobilized MacMillan Catalysts / 35	
	2.7	Polymer-immobilized Pyrrolidine Derivatives / 42	
	2.8	Other Polymer-immobilized Chiral Quaternary Ammonium Salts / 46	
	2.9	Polymer-immobilized Proline Derivatives / 46	
	2.10	Polymer-immobilized Peptides and Poly(amino acid)s / 50	
	2.11	Polymer-immobilized Chiral Acidic Organocatalysts / 50	
	2.12	Helical Polymers as Chiral Organocatalysts / 51	
	2.13	Cascade Reactions Using Polymer-immobilized Chiral Organocatalysts / 52	
	2.14	Conclusions / 54	
	Refer	ences / 56	
3	-	nmetric Synthesis Using Polymer-Immobilized ne Derivatives	63
	Miche	langelo Gruttadauria, Francesco Giacalone, and Renato Noto	
	3.1	Introduction / 63	
	3.2	Polymer-supported Proline / 66	
	3.3	Polymer-supported Prolinamides / 73	
	3.4	Polymer-supported Proline-Peptides / 75	
	3.5	Polymer-supported Pyrrolidines / 78	
	3.6	Polymer-supported Prolinol and Diarylprolinol Derivatives / 80	
	3.7	Conclusions and Outlooks / 84	
		ences / 85	
	Refer		
4	Pept	ide-Catalyzed Asymmetric Synthesis aki Kudo and Kengo Akagawa	91
4	<b>Pept</b> <i>Kazua</i>	ide-Catalyzed Asymmetric Synthesis aki Kudo and Kengo Akagawa	91
4	Pept	ide-Catalyzed Asymmetric Synthesis	91

	Others	sions and Outlooks / 119	
Chira	al Catal	Flow System using Polymer-Supported ysts uis and Eduardo García-Verdugo	125
5.1		ction / 125	
5.2	Asymm	netric Polymer-supported, Metal-based Catalysts agents / 132	
		Enantioselective Additions to C=O Groups / 132	
	5.2.2	Diels-Alder and Related Cycloaddition Reactions / 136	
	5.2.3	Enantioslective Cyclopropanation Reactions / 139	
	5.2.4	Reduction Reactions / 142	
	5.2.5	Oxidation Reactions / 143	
5.3	Polyme	er-supported Asymmetric Organocatalysts / 147	
5.4	Polyme	er-supported Biocatalysts / 151	
5.5	Conclu	sions / 152	
Refere	ences /	153	
Appr	oach	nesis on Polymer Support: A Combinatorial	157
-			
6.1 6.2		ction / 157 Synthesis of Complex Polyfunctional Molecules on Polyme t / 160	er
	6.2.1	Spirocyclic Compound Libraries / 160	
	6.2.2	Macrocyclic Compound Libraries / 165	
	6.2.3	Heterocyclic Compound Libraries / 168	
	6.2.4	Natural-product-inspired Compound Libraries / 176	
	6.2.5	Libraries Through Combinatorial Decoration of Natural Products / 184	
	6.2.6	Divergent Synthesis of Small Molecular Libraries / 188	
	6.2.7	Chiral Molecules Through Sequential Use of Polymer-supported Reagents / 192	
6.3	Conclu	sions / 194	
Refere	ences /	195	

5

6

7	with	hesis and Application of Helical Polymers  Macromolecular Helicity Memory 2  Iida and Eiji Yashima	01
	7.1 7.2	Introduction / 201  Macromolecular Helicity Memory / 203  7.2.1 Macromolecular Helicity Memory in Solution / 203  7.2.2 Macromolecular Helicity Memory in a Gel and a Solid / 213	
	7.3	Enantioselective Reaction Assisted by Helical Polymers with Helicity Memory / 218	
	7.4	Conclusions / 219	
	Refer	ences / 219	
8	Helic in As	(isocyanide)s, Poly(quinoxaline-2,3-diyl)s, and Related al Polymers Used as Chiral Polymer Catalysts symmetric Synthesis 2  Nagata and Michinori Suginome	23
	8.1	Introduction / 223	
	8.2	Asymmetric Synthesis of Poly(isocyanide)s / 224	
		8.2.1 Synthesis of Poly(isocyanide)s Bearing Chiral Side Chains / 224	
		8.2.2 Nonracemic Poly(isocyanide)s Without Chiral Pendant Groups / 239	
	8.3	Asymmetric Synthesis of Poly(quinoxaline)s / 244	
		8.3.1 Polymerization of 1,2-diisocyanobenzenes / 244	
		8.3.2 Preparation of Nonracemic Poly(quinoxaline)s / 246	
	8.4	Enantioselective Catalysis using Helical Polymers / 255	
		8.4.1 Chiral Polymer Catalysts with Chiral Groups in the Close Proximity of the Reaction Sites / 255	
		8.4.2 Chiral Polymer Catalysts with No Chiral Groups in the Proximity of the Reaction Sites / 258	
	8.5	Conclusions / 262	
	Refer	ences / 263	
9	Appl	hiral Biaryl Unit-Based Helical Polymers and Their ication to Asymmetric Catalysis 2 hi Maeda and Toshikazu Takata	67
	9.1	Introduction / 267	
	9.2	Synthesis of $C_2$ Chiral Unit-based Helical Polymers / 269	

		9.2.1	Use of $C_2$ Chiral Biaryl Moieties as Chirally Twisted Unthe Polymer Main Chain / 269	its in
		9.2.2	Synthesis of Stable Helical Polymers by the Fixation of Main-chain Conformation / 277	
	9.3	-	netric Reactions Catalyzed by Helical Polymer sts / 282	
	9.4	•	sions / 289	
		ences /		
10	Cata	lysts (N	•	293
	Hiroal	ki Sasai .	and Shinobu Takizawa	
	10.1	Introdu	ction / 293	
	10.2	Dendrii MACs	mer-Supported and Dendronized Polymer-supported / 294	
		10.2.1	Dendrimer-supported MACs [4] / 294	
		10.2.2	Dendronized Polymer-supported MACs [11] / 296	
	10.3	Nanopa	articles as Supports for Chiral Catalysts [13] / 302	
		10.3.1	Micelle-derived Polymer Supports [14] / 302	
		10.3.2	Monolayer-protected Au Cluster (Au-MPC)-supported Enantioselective Catalysts [21] / 307	
	10.4	The Ca	talyst Analog Approach [24] / 311	
	10.5	Immob	oridged Polymers as Heterogeneous Catalysts: An ilization Method for MACs Without Using Any t [26] / 314	
	10.6	Conclu	sion / 318	
1	Referei	nces / 3	19	
11	and	Their U	ctive Polymer and Dendrimer Synthesis se in Asymmetric Synthesis lu and Lin Pu	323
	11.1	Introdu	ction / 323	
	11.2		sis and Application of BINOL/BINAP-based Optically Activers / 324	ve
		11.2.1	Synthesis of BINOL-based Optically Active Polymers / 324	
		11.2.2	Application of BINOL-based Optically Active Polymers / 327	
		11.2.3	Synthesis and Application of a BINAP-containing Polymer / 347	

Х	CONT	ENTS		
		11.2.4	Synthesis of an Optically Active BINOL-BINAP-based Bifunctional Polymer and Application in Asymmetric Alkylation and Hydrogenation / 351	
	11.3	Synthes	sis and Application of Optically Active Dendrimers / 355	
		11.3.1	Synthesis of BINOL-based Dendrimers and Application in Asymmetric Alkylation / 355	
		11.3.2	Synthesis of Optically Active, Ephedrine-based Dendron Polymers / 358	ized
	11.4	Conclus	sions / 360	
	Ackno	wledgme	nt / 361	
]	Refere	nces / 30	61	
12	Asyr	nmetric	Polymerizations of <i>N</i> -Substituted	
		imides		365
	Kenjii	o Onimu	ra and Tsutomu Oishi	
	12.1	Introdu	ction / 365	
	12.2	Chiralit Olefins	y of 1-Mono- or 1,1-Disubstituted and 1,2-Disubstituted / 365	
	12.3	•	netric Polymerizations of Achiral <i>N</i> -Substituted iides / 368	
	12.4	Anionic	e Polymerization Mechanism of RMI / 371	
	12.5		netric Polymerizations of Chiral <i>N</i> -Substituted ides / 372	
	12.6	Structur	re and Absolute Stereochemistry of Poly(RMI) / 373	
	12.7	Asymm	etric Radical Polymerizations of N-Substituted Maleimides / 37	78
	12.8		Discrimination Using Poly(RMI) / 378 <sup>1</sup> H NMR Titration / 380	
		12.8.1	Optical Resolution Using Poly(RMI) / 381	
	12.9		sions / 384	
]	1-17	nces / 3		
13	Unite		f Hyperbranched Polymer Having Binaphthol cidative Cross-Coupling Polymerization	389
	13.1		ction / 389	
	13.2	Oxidati	ve Cross-coupling Reaction between 2-Naphthol Hydroxy-2-naphthoate / 391	
	13.3	Oxidati	ve Cross-coupling Polymerization Affording Linear naphthol) / 392	
	13.4	Oxidati	ve Cross-coupling Polymerization Leading	

		0011	ILIVIO	A.
13.5 13.6		uminescence Properties of Hyperbranched Polymers usions / 403	/ 400	
Refere	nces / 4	404		
•	<b>cally A</b> o o Nozaki	ctive Polyketones	4	107
14.1	Introdu	action / 407		
14.2	Asymn	metric Synthesis of Isotactic Poly(propylene-alt-co)	/ 409	
14.3	•	metric Synthesis of Isotactic Syndiotactic tyrene- <i>alt</i> -co) / 411		
14.4	-	netric Terpolymers Consisting of Two Kinds of Olef arbon Monoxide / 413	ìns	
14.5	Asymn	netric Polymerization of Other Olefins with CO / 4	14	
14.6	Chemic	cal Transformations of Optically Active Polyketones	/ 415	
14.7	Confor	rmational Studies on the Optically Active Polyketone	s / 416	
14.8	Conclu	usions / 419		
Refere	nces / 4	120		
Poly	mers fr	and Function of Chiral π-Conjugated rom Phenylacetylenes Takashi Kaneko, and Masahiro Teraguchi	4	123
15.1	Introdu	action / 423		
15.2				
	15.2.1	Synthesis of Chiral $\pi$ -Conjugated Polymers from Phenylacetylenes by Asymmetric-induced Polymer (AIP) and Helix-sense-selective Polymerization (Helix) and Achiral Phenylacetylenes / 425		
	15.2.2	(HSSP) of Three Types of Monomers RDHPA, RI and RDIPA, Scheme 15.4a / 427	OAPA,	
	15.2.3	Modified HSSP / 432		
	15.2.4	Functions of One-handed Helical Polyphenylacety Prepared by HSSP / 434	lenes	
15.3	Chiral	Desubstitution of Side Groups in Membrane State /	439	
	15.3.1	Polymer Reaction in Membrane State(RIM) / 439	ı	
	15.3.2	Reaction in One-handed Helical Polymer Membra Synthesis of One-handed Helical Polymers with no Groups and no Chiral Carbons / 439		ide

Reaction in Polystyrene Monolith: Synthesis of Chiral Porous Materials / 444

14

15

15.3.3

	15.4	Synthes	sis of Chiral Polyradicals / 446			
		•	Molecular Design of Optically Active Helical Polyradicals /	446		
		15.4.2				
		15.4.3	Synthesis of Chiral Polyradicals via HSSP of Achiral Monomers / 450			
I	Referei	nces / 4	54			
16		ereoger pounds	nic Oligomers, Polymers, and Related Cyclic	457		
		•	saki and Yoshiki Chujo			
	16.1	Introduction / 457				
	16.2		ogenic Oligomers Containing Chiral "P" Atoms Main Chain / 458			
		16.2.1	P-Stereogenic Tetraphosphines Containing Two Chiral "P" Atoms / 458			
		16.2.2	P-Stereogenic Hexaphosphines Containing Four Chiral "P" Atoms / 461			
		16.2.3	P-Stereogenic Oligomers Containing 6, 8, and 12 Chiral "P" Atoms / 464			
	16.3	P-Stere Chain	ogenic Polymers Containing Chiral "P" Atoms in the Main / 470	1		
		16.3.1	P-Stereogenic Polymers Containing Chiral "P" Atoms in the Repeating Unit of the Main Chain / 470			
		16.3.2	Optically Active Dendrimers Containing the P-Chiral Bisphosphine Unit as the Core / 473			
		16.3.3	Helical Polymers Containing Chiral "P" Atoms in the Terminal Unit / 473			
	16.4 Cyclic Phosphines Using P-Stereogenic as Building Blocks / 475		Phosphines Using P-Stereogenic Oligomers ding Blocks / 475			
		16.4.1	Stereospecific Synthesis of <i>trans</i> -1,4-Diphosphacyclohexane / 475			
		16.4.2	Synthesis of 1,4,7,10-Tetraphosphacyclodocecane, 12-Phosphacrown-4 / 478			
		16.4.3	Synthesis of 18-Diphosphacrown-6 / 480			
	16.5	Conclu	sions / 485			
I	Referei	nces / 4	85			
IND	EX			489		