

Contents

<i>Foreword</i>	<i>xiii</i>
<i>Preface</i>	<i>xv</i>
<i>John Boor, Jr. (1930–1974)</i>	<i>xvii</i>

1

HIGHLIGHTS OF ZIEGLER–NATTA CATALYSTS AND POLYMERIZATIONS

I. Highlights	1
II. Collected Reviews	12
References	12

2

GENESIS OF ZIEGLER–NATTA CATALYSTS

I. Scientific and Commercial Importance	19
II. Historical Origins	21
III. Anticipation of the Catalyst and Contemporary Discoveries	26
IV. The Golden Age of Polymer Science	28
References	29

3

DEFINITIONS, STEREOCHEMISTRY, EXPERIMENTAL METHODS, AND COMMERCIAL POLYMERS

I. Introduction	32
II. Definition of Ziegler–Natta Catalysts	33
III. Stereochemical Structures of Polymers and Methods of Characterization	35
IV. Experimental Methods	61
V. Commercial Polymers	67
References	77

4

CHEMICAL DESCRIPTION OF ZIEGLER-NATTA CATALYSTS FOR OLEFINS

I.	Introduction	80
II.	Factors Determining Behavior of Catalysts for Olefins	81
III.	Some Important Classes of Catalysts for Olefins	108
IV.	Conclusion	124
	References	125

5

THE CHEMICAL DESCRIPTION OF CATALYSTS FOR CONJUGATED DIENES

I.	Introduction	130
II.	Factors Determining Isomerism	131
III.	Important Catalysts Identified for Specific Conjugated Dienes	141
IV.	Conclusion	148
	References	149

6

INITIAL PHYSICAL STATE OF THE CATALYST

I.	Introduction	154
II.	Importance of the Physical State of the Catalyst	154
III.	Soluble Catalyst	156
IV.	Colloidal Catalysts	156
V.	Heterogenous Catalysis Including Supported Types	160
VI.	Conclusion	165
	References	166

7

PHYSICAL STATE OF THE POLYMER DURING POLYMERIZATION

I.	Introduction	168
II.	The Solution Process	169
III.	The Slurry Process	172
IV.	Vapor Phase Process	173
V.	Conclusion	178
	References	178

8

GROWTH OF THE POLYMER PARTICLE

I.	Introduction	180
II.	Replication	181
III.	Architecture of TiCl_3 Particles	184
IV.	How Does the Polymer Particle Grow?	190
V.	Practical Importance	209
VI.	Conclusion	211
	References	211

9

MODIFICATION OF ZIEGLER-NATTA CATALYSTS BY THIRD COMPONENTS

I.	Introduction	213
II.	Discussion of Donors: Types of Third Components Added	215
III.	Conclusion	239
	References	240

10

TERMINATION OF POLYMER CHAIN GROWTH

I.	Introduction	244
II.	Chain Termination by Organic and Inorganic Compounds	245
III.	Chain Termination by Metal Alkyls	247
IV.	Chain Termination by Molecular Hydrogen	251
V.	Chain Termination by Unsaturated Hydrocarbons	256
VI.	Chain Termination by Thermal Cleavage	258
VII.	Chain Termination by Mechanical Forces	259
	References	259

11

OXIDATION STATE OF CATALYSTS AND ACTIVE CENTERS

I.	Introduction	261
II.	Catalysts Containing Selected Period 2 Transition Metal Salts	262
III.	Conclusion	276
	References	277

12

METAL ALKYL-FREE CATALYSTS

I.	Introduction	279
II.	Phillips and Standard of Indiana Catalysts	280
III.	Metal Alkyl-Free Catalysts Discovered after 1955	285
IV.	Relationship to Ziegler-Natta Catalysts	316
	References	318

13

MECHANISMS FOR INITIATION AND PROPAGATION OF OLEFINS

I.	Introduction	325
II.	Nomenclature	326
III.	Proposed Mechanisms	327
IV.	Experimental Evidence	341
V.	Conclusion	361
	References	362

14

MECHANISMS FOR INITIATION AND PROPAGATION OF DIENES

I.	Introduction	366
II.	Proposed Mechanisms	366
III.	Experimental Evidence	369
IV.	Conclusion	379
	References	380

15

MECHANISMS FOR STEREOCHEMICAL CONTROL OF α -OLEFINS

I.	Introduction	382
II.	Mode of Addition	383
III.	Isotactic Propagation	390
IV.	Syndiotactic Propagation	411
V.	Steric Purity of Isotactic and Syndiotactic Polypropylenes	418
VI.	Conclusion	419
	References	419

16

MECHANISMS FOR STEREOCHEMICAL CONTROL OF CONJUGATED AND NONCONJUGATED DIENES

I. Introduction	422
II. Conjugated Dienes	422
III. Nonconjugated Dienes	436
IV. Conclusion	439
References	440

17

MECHANISMS FOR STEREOCHEMICAL CONTROL OF STEREOSELECTIVE AND STEREOELECTIVE ISOTACTIC PROPAGATIONS

I. Introduction	442
II. Stereoselection	443
III. Stereoelection	448
IV. Proposed Mechanisms	454
References	462

18

KINETICS

I. Introduction	464
II. Basic Kinetic Results	465
III. Proposed Kinetic Models and Schemes	474
IV. Operational Factors That Can Affect Kinetic Results	480
V. Growth of Polymer Chain and Particle	490
VI. Conclusion	508
References	508

19

POLYMERIZATION OF MONOMERS

I. Introduction	512
II. Ethylene	512
III. 1-Olefins	513
IV. 1,1-Disubstituted Ethylene	520
V. 1,2-Disubstituted Ethylenes	521
VI. Cycloolefins	523
VII. Bicyclo[n.1.0]alkanes	531
VIII. Polar Monomers	531

IX.	Allenes	539
X.	Acetylenes	540
XI.	Conjugated Cyclic and Acyclic Dienes	543
XII.	Nonconjugated Acyclic and Cyclic Diolefins	547
	References	554

20

COPOLYMERIZATIONS

I.	Introduction	563
II.	Copolymerization Equation and Nomenclature	564
III.	Experimental Control over the Architecture of Copolymer Chains	565
IV.	Copolymerizations of Selected Comonomer Pairs	576
V.	Conclusion	583
	References	584

21

BLOCK POLYMERIZATIONS

I.	Introduction	587
II.	Pioneering Work	588
III.	Other Studies Aimed at Block Polymers	595
IV.	Conclusion	598
	References	600

22

OTHER USES OF THE ZIEGLER-NATTA CATALYST

I.	Introduction	602
II.	Radical and Cationic Polymerizations	602
III.	Metathesis of Acyclic and Cyclic Olefins	603
IV.	Oligomerization of Olefins and Acetylenes	604
V.	Isomerization of Olefins	606
VI.	Hydrogenation of Olefins and Unsaturated Polymers	607
VII.	Alkylation of Aromatic Nuclei by Unsaturated Systems	608
VIII.	Examples of Other Competing Side Reactions	608
	References	609

23

FINAL COMMENTS AND OUTLOOK

		611
	<i>Supplementary Bibliography</i>	615
	<i>Subject Index</i>	659