

## Contents

<b>Preface</b>	XV
<b>List of Contributors</b>	XIX

<b>1</b>	<b>Anionic Vinyl Polymerization</b>	<b>1</b>
	<i>Durairaj Baskaran and Axel H.E. Müller</i>	
1.1	Introduction	1
1.1.1	The Discovery of Living Anionic Polymerization	1
1.1.2	Consequences of Termination- and Transfer-Free Polymerization	2
1.1.3	Suitable Monomers	5
1.2	Structure of Carbanions	6
1.3	Initiation	7
1.3.1	Anionic Initiators	8
1.3.2	Experimental Considerations	11
1.4	Mechanism of Styrene and Diene Polymerization	11
1.4.1	Polymerization of Styrene in Polar Solvents: Ions and Ion Pairs	11
1.4.2	Contact and Solvent-Separated Ion Pairs	13
1.4.3	Polymerization of Styrene in Nonpolar Solvents: Aggregation Equilibria	15
1.4.3.1	Polymerization in Pure Solvents	15
1.4.3.2	Polymerization in Nonpolar Solvent in the Presence of Ligands	16
1.4.4	Anionic Polymerization of Dienes in Nonpolar Solvent	18
1.4.4.1	Kinetics	18
1.4.4.2	Regiochemistry	19
1.4.5	Architectural Control Using Chain-End Functionalization	20
1.5	Mechanism of Anionic Polymerization of Acrylic Monomers	20
1.5.1	Side Reactions of Alkyl (Meth)acrylate Polymerization	22
1.5.2	Alkyl (Meth)acrylate Polymerization in THF	24
1.5.2.1	Propagation by Solvated Ion Pairs	24
1.5.2.2	Association of Enolate Ion Pairs and Their Equilibrium Dynamics	25
1.5.2.3	Effect of Dynamics of the Association Equilibrium on the MWD	27
1.5.3	Modification of Enolate Ion Pairs with Ligands: Ligated Anionic Polymerization	29
1.5.3.1	Lewis Base ( $\sigma$ -Type) Coordination	29

1.5.3.2	Lewis Acid ( $\mu$ -Type) Coordination	30
1.5.4	Metal-Free Anionic Polymerization	32
1.5.4.1	Group Transfer Polymerization (GTP)	32
1.5.4.2	Tetraalkylammonium Counterions	35
1.5.4.3	Phosphorous-Containing Counterions	36
1.5.5	Polymerization of Alkyl (Meth)acrylates in Nonpolar Solvents	37
1.5.5.1	$\mu$ -Type Coordination	38
1.5.5.2	$\sigma$ , $\mu$ -Type Coordination	40
1.5.6	Coordinative-Anionic Initiating Systems	40
1.5.6.1	Aluminum Porphyrins	40
1.5.6.2	Metallocenes	41
1.5.7	Polymerization of <i>N,N</i> -Dialkylacrylamides	41
1.6	Some Applications of Anionic Polymerization	43
1.7	Conclusions and Outlook	45
	References	46
<b>2</b>	<b>Carbocationic Polymerization</b>	<b>57</b>
	<i>Priyadarsi De and Rudolf Faust</i>	
2.1	Introduction	57
2.2	Mechanistic and Kinetic Details of Living Cationic Polymerization	58
2.3	Living Cationic Polymerization	60
2.3.1	Monomers and Initiating Systems	61
2.3.2	Additives in Living Cationic Polymerization	61
2.3.3	Living Cationic Polymerization: Isobutylene (IB)	62
2.3.4	$\beta$ -Pinene	64
2.3.5	Styrene (St)	64
2.3.6	<i>p</i> -Methylstyrene ( <i>p</i> -MeSt)	65
2.3.7	<i>p</i> -Chlorostyrene ( <i>p</i> -ClSt)	66
2.3.8	2,4,6-Trimethylstyrene (TMeSt)	66
2.3.9	<i>p</i> -Methoxystyrene ( <i>p</i> -MeOSt)	66
2.3.10	$\alpha$ -Methylstyrene ( $\alpha$ MeSt)	67
2.3.11	Indene	67
2.3.12	<i>N</i> -Vinylcarbazol	68
2.3.13	Vinyl Ethers	68
2.4	Functional Polymers by Living Cationic Polymerization	69
2.4.1	Functional Initiator Method	69
2.4.2	Functional Terminator Method	71
2.5	Telechelic Polymers	73
2.6	Macromonomers	75
2.6.1	Synthesis Using a Functional Initiator	76
2.6.2	Synthesis Using a Functional Capping Agent	77
2.6.2.1	Chain-End Modification	79
2.6.2.2	Block Copolymers	79
2.7	Linear Diblock Copolymers	80

2.8	Linear Triblock Copolymers	83
2.8.1	Synthesis Using Difunctional Initiators	83
2.8.2	Synthesis Using Coupling Agents	84
2.9	Block Copolymers with Nonlinear Architecture	85
2.9.1	Synthesis of $A_nB_n$ Hetero-Arm Star-Block Copolymers	86
2.9.2	Synthesis of AA B, ABB', and ABC Asymmetric Star-Block Copolymers Using Furan Derivatives	88
2.9.3	Block Copolymers Prepared by the Combination of Different Polymerization Mechanisms	88
2.9.3.1	Combination of Cationic and Anionic Polymerization	88
2.9.3.2	Combination of Living Cationic and Anionic Ring-Opening Polymerization	90
2.9.3.3	Combination of Living Cationic and Radical Polymerization	91
2.10	Branched and Hyperbranched Polymers	92
2.11	Surface Initiated Polymerization – Polymer Brushes	93
2.12	Conclusions	94
	References	94
<b>3</b>	<b>Radical Polymerization</b>	<b>103</b>
	<i>Krzysztof Matyjaszewski</i>	
3.1	Introduction	103
3.2	Typical Features of Radical Polymerization	104
3.2.1	Kinetics	104
3.2.2	Copolymerization	107
3.2.3	Monomers	107
3.2.4	Initiators and Additives	107
3.2.5	Typical Conditions	108
3.2.6	Commercially Important Polymers by RP	108
3.3	Controlled Reversible-Deactivation Radical Polymerization	110
3.3.1	General Concepts	110
3.3.2	Similarities and Differences Between RP and CRP	111
3.4	SFRP: NMP and OMRP Systems – Examples and Peculiarities	112
3.4.1	OMRP Systems	114
3.4.2	Monomers and Initiators	114
3.4.3	General Conditions	114
3.4.4	Controlled Architectures	115
3.5	ATRP – Examples and Peculiarities	115
3.5.1	Basic ATRP Components	117
3.5.1.1	Monomers	117
3.5.1.2	Transition Metal Complexes as ATRP Catalysts	117
3.5.1.3	Initiators	120
3.5.2	Conditions	122
3.5.3	Mechanistic Features	125
3.5.4	Controlled Architectures	125

3.6	Degenerative Transfer Processes and RAFT	126
3.5.6.1	Monomers and Initiators	128
3.5.6.2	Transfer Agents	128
3.6.3	Controlled Architectures	129
3.7	Relative Advantages and Limitations of SFRP, ATRP, and DT Processes	129
3.7.1	Reactivity Orders in Various CRP Systems	131
3.7.2	Interrelation and Overlap Between Various CRP Systems	132
3.8	Controlled Polymer Architectures by CRP: Topology	133
3.8.1	Linear Chains	134
3.8.2	Star-Like Polymers	135
3.8.3	Comb-Like Polymers	137
3.8.4	Branched and Hyperbranched Polymers	138
3.8.5	Dendritic Structures	139
3.8.6	Polymer Networks and Microgels	140
3.8.7	Cyclic Polymers	141
3.9	Chain Composition	141
3.9.1	Statistical Copolymers	141
3.9.2	Segmented Copolymers (Block, Grafts and Multisegmented Copolymers)	142
3.9.2.1	Block Copolymers by a Single CRP Method	142
3.9.2.2	Block Copolymers by Combination of CRP Methods	142
3.9.2.3	Block Copolymerization by Site Transformation and Dual Initiators	142
3.9.2.4	Multisegmented Block Copolymers	144
3.9.2.5	Stereoblock Copolymers	145
3.9.3	Graft Copolymers	145
3.9.4	Periodic Copolymers	147
3.9.5	Gradient Copolymers	147
3.9.6	Molecular Hybrids	148
3.9.7	Templated Systems	148
3.10	Functional Polymers	149
3.10.1	Polymers with Side Functional Groups	150
3.10.2	End Group Functionality: Initiators	150
3.10.3	End Group Functionality through Conversion of Dormant Chain End	151
3.11	Applications of Materials Prepared by CRP	152
3.11.1	Polymers with Controlled Compositions	152
3.11.2	Polymers with Controlled Topology	152
3.11.3	Polymers with Controlled Functionality	153
3.11.4	Hybrids	153
3.12	Outlook	153
3.12.1	Mechanisms	154
3.12.2	Molecular Architecture	154
3.12.3	Structure–Property Relationship	155

Acknowledgments	156
References	156

<b>4</b>	<b>Living Transition Metal-Catalyzed Alkene Polymerization: Polyolefin Synthesis and New Polymer Architectures</b>	<b>167</b>
	<i>Joseph B. Edson, Gregory J. Domski, Jeffrey M. Rose, Andrew D. Bolig, Maurice Brookhart, and Geoffrey W. Coates</i>	
4.1	Introduction	167
4.2	Living $\alpha$ -Olefin Polymerization	169
4.2.1	Metallocene-Based Catalysts	170
4.2.2	Catalysts Bearing Diamido Ligands	171
4.2.3	Catalysts Bearing Diamido Ligands with Neutral Donors	171
4.2.4	Amine-Phenolate and Amine-Diol Titanium and Zirconium Catalysts	173
4.2.5	Monocyclopentadienylzirconium Amidinate Catalysts	176
4.2.6	Pyridylamidohafnium Catalysts	177
4.2.7	Titanium Catalysts for Styrene Homo- and Copolymerization	178
4.2.8	Tripodal Trisoxazoline Scandium Catalysts	179
4.2.9	Late Transition Metal Catalysts	179
4.3	Living Propylene Polymerization	182
4.3.1	Vanadium Acetylacetonate Catalysts	183
4.3.2	Metallocene-Based Catalysts	185
4.3.3	Catalysts Bearing Diamido Ligands	186
4.3.4	Bis(phenoxyimine)titanium Catalysts	187
4.3.5	Bis(phenoxyketimine)titanium Catalysts	190
4.3.6	Amine Bisphenolate Zirconium Catalysts	191
4.3.7	Monocyclopentadienylzirconium Amidinate Catalysts	192
4.3.8	Pyridylamidohafnium Catalysts	194
4.3.9	Late Transition Metal Catalysts	195
4.4	Living Polymerization of Ethylene	196
4.4.1	Non-Group 4 Early Metal Polymerization Catalysts	197
4.4.2	Bis(phenoxyimine)titanium Catalysts	199
4.4.3	Bis(phenoxyketimine)titanium Catalysts	201
4.4.4	Titanium Indolide–Imine Catalysts	201
4.4.5	Bis(enaminoketonato)titanium Catalysts	202
4.4.6	Aminopyridinatozirconium Catalysts	202
4.4.7	Tris(pyrazolyl)borate Catalysts	203
4.4.8	Late Transition Metal Catalysts	203
4.5	Living Nonconjugated Diene Polymerization	206
4.5.1	Vanadium Acetylacetonate Catalysts	207
4.5.2	Bis(phenoxyimine)titanium Catalysts	207
4.5.3	Cyclopentadienyl Acetamidinate Zirconium Catalysts	208
4.5.4	Late Transition Metal Catalysts	208
4.6	Living Homo- and Copolymerizations of Cyclic Olefins	209
4.6.1	Norbornene Homopolymerization	209

4.6.2	Copolymers of Norbornene/Ethylene and Cyclopentene/Ethylene	210
4.6.2.1	Non-Group 4 Early Transition Metal Catalysts	210
4.6.2.2	Group 4 Metallocene-Based Catalysts	210
4.6.2.3	Titanium Catalysts for Living Ethylene–Cyclic Olefin Copolymerization	211
4.6.2.4	Palladium $\alpha$ -Diimine Catalysts	212
4.7	Random Copolymers	212
4.7.1	Random Copolymers Incorporating Polar Monomers	212
4.8	Block Copolymers	213
4.8.1	Block Copolymers Containing Poly( $\alpha$ -olefin) Blocks	213
4.8.2	Block Copolymers Containing Polypropylene Blocks	216
4.8.2.1	Isotactic Polypropylene-Containing Block Copolymers	216
4.8.2.2	Syndiotactic Polypropylene-Containing Block Copolymers	218
4.8.2.3	Atactic Polypropylene-Containing Block Copolymers	220
4.8.3	Polyethylene-Containing Block Copolymers	221
4.8.4	Norbornene- and Cyclopentene-Containing Block Copolymers	222
4.8.5	Block Copolymers Containing Blocks Derived from 1,5-Hexadiene Polymerization	224
4.8.6	Block Copolymers Containing Blocks Derived from Polar Monomers	226
4.9	Outlook and Summary	231
	References	232
<b>5</b>	<b>Living Ring-Opening Polymerization of Heterocyclic Monomers</b>	<b>241</b>
	<i>Stanislaw Penczek, Marek Cypryk, Andrzej Duda, Przemyslaw Kubisa, and Stanislaw Słomkowski</i>	
5.1	Introduction	241
5.2	Anionic and Coordination Living Ring-Opening Polymerization (LROP)	246
5.2.1	Initiation in the Anionic LROP	248
5.2.2	Propagation in the Anionic LROP	249
5.2.2.1	Polymerization of O- and S-Heterocyclic Monomers	249
5.2.2.2	Polymerization of Si-, N-, and P-Heterocyclic Monomers	253
5.2.3	Coordination Polymerization	259
5.2.4	Organocatalytic ROP of Cyclic Esters	265
5.2.5	Transfer Processes in the LROP	267
5.2.6	Departures from the Livingness	273
5.3	Cationic CROP and LROP	274
5.3.1	Cationic ROP of Tetrahydrofuran (THF)	274
5.3.2	Propagation in the Cationic ROP	276
5.3.3	Macroion–Macroester Interconversions in the Cationic ROP	278
5.3.4	Cationic ROP of Cyclic Imino Ethers (Oxazolines) and Cyclic Thioesters	280
5.3.5	Cationic ROP of Cyclosiloxanes	282
5.3.6	Activated Monomer Cationic ROP of Cyclic Monomers	283

5.4	CROP and LROP Conducted in Dispersions	287
5.5	Conclusion	289
	References	289
<b>6</b>	<b>Living Ring-Opening Metathesis Polymerization</b>	<b>297</b>
	<i>Christopher W. Bielawski and Robert H. Grubbs</i>	
6.1	Overview of Ring-Opening Metathesis Polymerization (ROMP)	297
6.1.1	Introduction	297
6.1.2	ROMP Essentials: Mechanism and Thermodynamics	297
6.1.3	Living Ring-Opening Metathesis Polymerization	300
6.2	Initiators for Living ROMP	302
6.2.1	Historical Aspects	302
6.2.2	Ill-Defined Initiators	302
6.2.3	Titanium	304
6.2.4	Tantalum	307
6.2.5	Tungsten	309
6.2.6	Molybdenum	313
6.2.7	Ruthenium	318
6.3	Applications of Polymers Synthesized Using ROMP: From Novel Materials to Commercial Products	326
6.3.1	Selected Applications for Polymers Synthesized Using ROMP	327
6.3.2	Commercial Polymers Synthesized Using ROMP	331
6.4	Challenges and Perspectives for the Future	333
6.4.1	Development of New Initiators	333
6.4.2	Polymerization of “New” and “Old” Monomers	334
6.5	Conclusion	335
	Acknowledgments	336
	References	336
<b>7</b>	<b>Macromolecular Architectures by Living and Controlled/ Living Polymerizations</b>	<b>343</b>
	<i>Nikos Hadjichristidis, Marinos Pitsikalis, Hermis Iatrou, and Georgios Sakellariou</i>	
7.1	Introduction	343
7.2	Star Polymers	344
7.2.1	Symmetric Stars	344
7.2.1.1	Multifunctional Initiators (MFIs)	344
7.2.1.2	Multifunctional Linking Agents (MFLAs)	350
7.2.1.3	Difunctional Monomers (DFMs)	355
7.2.2	Star-Block Copolymers	359
7.2.3	Asymmetric Stars	362
7.2.3.1	Molecular Weight Asymmetry	363
7.2.3.2	Topological Asymmetry	369
7.2.4	Miktoarm Star Polymers	370
7.3	Comb Polymers	379
7.3.1	“Grafting Onto” Methods	381

7.3.2	“Grafting from” Methods	382
7.3.3	“Grafting Through” or Macromonomer Method	384
7.4	Cyclic Polymers	393
7.4.1	Cyclic Polymers from Precursors with Homodifunctional Groups	395
7.4.2	Cyclic Homopolymers	395
7.4.3	Cyclic Block Copolymers	399
7.5	Dendritic Polymers	400
7.5.1	Dendrimers	401
7.5.2	Dendritic Polymers	408
7.6	Complex Macromolecular Architectures	416
7.6.1	$\omega$ -Branched Polymers	416
7.6.2	$\alpha,\omega$ -Branched Polymers	417
7.6.3	Hyperbranched and Dendrigrraft Polymers	420
7.6.4	Other Complex Architectures	426
7.7	Applications	431
7.8	Conclusions	436
	References	438
<b>8</b>	<b>Synthesis of Block and Graft Copolymers</b>	<b>445</b>
	<i>Constantinos Tsitsilianis</i>	
8.1	Introduction	445
8.2	Principles of Block Copolymerization	446
8.2.1	AB by Anionic Polymerization	447
8.2.2	AB by Cationic Polymerization	448
8.2.3	AB by Controlled Radical Polymerization	450
8.2.3.1	AB by ATRP	450
8.2.3.2	AB by NMP	451
8.2.3.3	AB by RAFT	451
8.2.4	AB by Combination of Methods	452
8.2.4.1	Site-Transformation Reactions	452
8.2.4.2	By Using Dual Initiator	454
8.2.5	AB by Coupling Reactions	455
8.3	ABA Triblock Copolymers	457
8.3.1	Synthetic Strategies	457
8.3.2	ABA by Anionic Polymerization	459
8.3.3	ABA by GTP	461
8.3.4	ABA by Cationic Polymerization	462
8.3.5	ABA by Controlled Radical Polymerization	463
8.3.6	ABA by Combination of Methods	465
8.4	$(AB)_n$ Linear Multiblock Copolymers	466
8.5	ABC Triblock Terpolymers	466
8.5.1	Synthetic Strategies	467
8.5.2	ABC by Anionic Polymerization	468
8.5.3	ABC by GTP	471



8.5.4	ABC by Cationic Polymerization	472
8.5.5	ABC by Controlled Radical Polymerization	472
8.5.6	ABC by Combination of Methods	473
8.6	Synthesis of ABCA Tetra- and ABCBA Pentablock Terpolymers	474
8.7	Synthesis of ABCD Quaterpolymers	475
8.8	Graft Copolymers	476
8.8.1	Synthetic Strategies	477
8.8.2	A-g-B Graft Copolymers	478
8.8.3	Model Graft-Like Architectures	483
8.9	Applications	486
8.10	Concluding Remarks	488
	References	488
<b>9</b>	<b>Morphologies in Block Copolymers</b>	<b>493</b>
	<i>Volker Abetz, Adriana Boschetti-de-Fierro, and Jean-François Gohy</i>	
9.1	Introduction	493
9.2	Block Copolymers in Bulk State	494
9.2.1	Theoretical Descriptions of Block Copolymer Morphologies in the Bulk State	495
9.2.2	Experimental Results on the Morphological Properties of Block Copolymers in the Bulk State	500
9.3	Block Copolymer Thin Films	505
9.3.1	General Concepts of Block Copolymer Thin Films	505
9.3.2	Controlled Self-Assembly in Block Copolymer Thin Films	507
9.3.2.1	Interactions with Air and Substrate Interfaces	507
9.3.2.2	Alignment by External Fields	511
9.3.2.3	Crystallization	513
9.4	Block Copolymer Micelles	516
9.4.1	General Concepts of Block Copolymer Micelles	516
9.4.2	Block Copolymer Micelles Containing Metal–Ligand Complexes	520
9.4.3	Multicompartment Micelles Made from ABC Triblock Terpolymers	530
9.4.3.1	Micelles with a Compartmentalized Core	530
9.4.3.2	Micelles with a Compartmentalized Corona	536
9.5	Applications	539
9.6	Summary and Outlook	542
	References	544
<b>10</b>	<b>Industrial Applications</b>	<b>555</b>
	<i>Dale L. Handlin, Jr., David R. Hansen, Kathryn J. Wright, and Scott R. Trenor</i>	
10.1	Introduction	555
10.2	Synthesis of Anionic Styrenic Block Copolymers	561
10.3	Adhesives and Sealants	564
10.4	Compounding Applications	568
10.4.1	Raw Material Selection	568

**XIV** | Contents

10.4.2	Processing and Forming	573
10.4.3	Automotive	575
10.4.4	Wire and Cable	577
10.4.5	Medical	578
10.4.6	Soft-Touch Overmolding	578
10.4.7	Ultrasoft Compounds	579
10.4.8	Elastic Films and Fibers	579
10.5	Polymer Modification	580
10.6	Cross-Linked Systems	582
10.6.1	SBC-Based Dynamic Vulcanizates	582
10.6.2	Flexographic Printing Plates	583
10.7	Bitumen Modification	584
10.7.1	Paving	584
10.7.2	Road Marking	587
10.7.3	Roofing	588
10.8	Footwear	589
10.9	Viscosity Modification and Other Highly Diluted SBC Applications	590
10.9.1	Viscosity Index Improvers	590
10.9.2	Oil Gels	591
10.10	Emerging Technology in Block Copolymers	591
10.10.1	Recycling Compatibilization	591
10.10.2	PVC and Silicone Replacement	592
10.10.3	Sulfonated Block Copolymers	592
10.10.4	Methacrylate and Acrylate Block Copolymers by Anionic Polymerization	593
10.10.5	Styrene-Isobutylene-Styrene (SiBS) via Cationic Polymerization	596
10.10.6	Commercial Uses of Other Controlled Polymerized Polymers	596
	References	599

**Index** 605