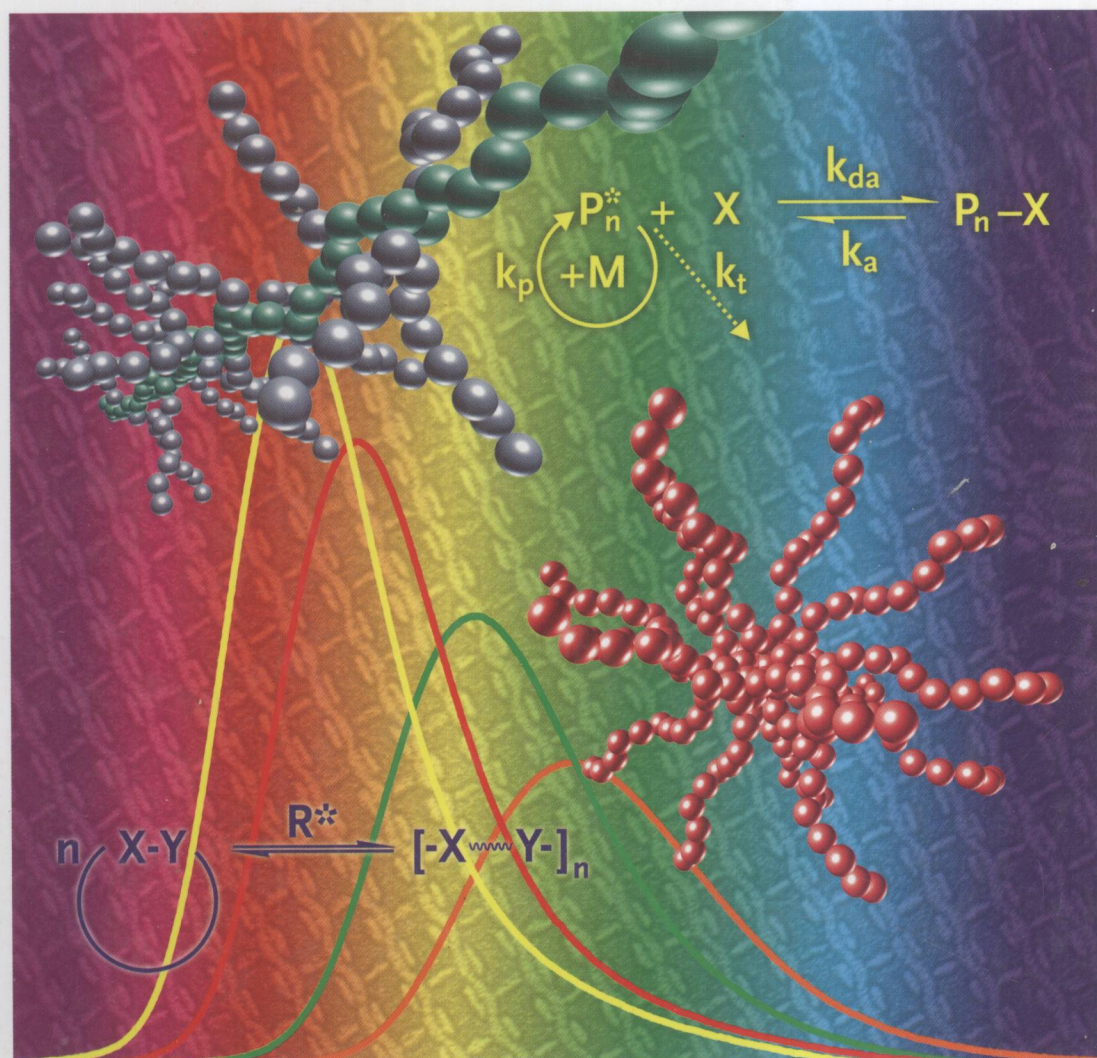


Edited by Axel H.E. Müller  
and Krzysztof Matyjaszewski

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# Controlled and Living Polymerizations

From Mechanisms to Applications



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# Controlled and Living Polymerizations

Methods and Materials

*Edited by*  
*Axel H.E. Müller*  
*and Krzysztof Matyjaszewski*



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## The Editors

**Prof. Axel H.E. Müller**

Universität Bayreuth  
Makromolekulare Chemie II  
Universitätsstr. 30  
95447 Bayreuth

**Prof. Krzysztof Matyjaszewski**

Carnegie Mellon University  
Dept. of Chemistry  
4400 Fifth Ave  
Pittsburgh PA 15213  
USA

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*and Krzysztof Matyjaszewski*

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## Preface: Controlled and Living Polymerizations

The discovery of living anionic polymerization and subsequently other controlled/living polymerizations has had tremendous impact on polymer and materials science. It facilitated major developments not only in synthetic polymer chemistry but also in polymer physics as it opened an avenue to the preparation of well-defined polymers with precisely designed molecular architectures and nanostructured morphologies. As an example, block copolymers synthesized via sequential monomer addition by Szwarc *et al.* more than 50 years ago [1] have inspired a generation of polymer physicists due to their potential to self-organize in bulk or solution. They were successfully commercialized as thermoplastic elastomers, compatibilizers, surfactants, or components of medical and personal care products, to name just a few applications. Thermoplastic elastomers, first commercialized under the trade name Kraton®, are landmark materials made by living anionic polymerization and they are applied in many compounding applications, including footwear, pressure-sensitive adhesives, cables, soft-touch overmolding, cushions, lubricants, gels, coatings, or in flexographic printing and road marking. It is anticipated that materials made by other controlled/living processes will lead to more applications with even larger market impact. Many details on the current and potential future applications of polymers made by controlled/living polymerization can be found in all chapters of this book.

The term *living polymer* was coined by Michael Szwarc to describe the products of the anionic polymerization of styrene initiated by electron transfer in tetrahydrofuran [1, 2]. In this context, “living” denotes the ability of a polymer chain to further add monomer after the initial batch of monomer has been consumed, and this means that the polymer chains do not undergo irreversible chain breaking reactions, such as termination or chain transfer. The IUPAC Gold Book [3] defines “living polymerization” as *a chain polymerization from which chain transfer and chain termination are absent*. It adds (although this is not part of the definition) the following: *In many cases, the rate of chain initiation is fast compared with the rate of chain propagation, so that the number of kinetic-chain carriers is essentially constant throughout the polymerization*. Typically, such a process should lead to a very narrow (Poisson) molecular weight distribution

(MWD). However, a slow initiation process can have a considerable impact on the molecular weights achieved and on the MWD.

It has been discussed how strict one should regard the absence of termination and transfer. For example, it is impossible to completely suppress termination in radical polymerization. Thus, Szwarc later modified his definition [4] saying that *a polymerization is living when the resulting polymer retains its integrity for a sufficiently long time to allow the operator to complete its task, whether a synthesis or any desired observation or measurement. Even in that time some decomposition or isomerization may occur, provided it is virtually undetectable and does not affect the results.*

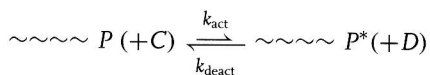
The term *controlled polymerization* introduced by us in 1987 [5] can be defined as a synthetic method to prepare polymers, which are well-defined with respect to topology (e.g., linear, star-shaped, comb-shaped, dendritic, and cyclic), terminal functionality, composition, and arrangement of comonomers (e.g., statistical, periodic, block, graft, and gradient), and which have molecular weights predetermined by the ratio of concentrations of reacted monomer to introduced initiator, as well as a designed (not necessarily narrow) MWD.

Thus, a living polymerization is not always controlled and a controlled polymerization is not always strictly living, according to the definitions given above. In the ideal case, a living polymerization is also controlled; however, in some systems such as in a radical polymerization, termination can never be entirely avoided but its contribution can be sometimes significantly reduced.

The feature of livingness was discovered in carbanionic polymerization in 1956. Many efforts were made in other polymerization methodologies to achieve a level of control attainable in living carbanionic polymerization. However, it took nearly 20 years until living cationic ring-opening polymerization was developed (living anionic ring-opening polymerization was known already for some time). Group transfer polymerization (GTP; a process close to anionic polymerization) was reported in 1983 and the living carbocationic polymerization in 1984. Subsequently, living ring-opening metathesis polymerization (ROMP) was reported in 1986 and various controlled/living radical polymerization mechanisms were reported in the 1990s. Finally, even coordination polymerization of olefins was made living.

It is intriguing that almost all new controlled/living systems have one common feature, which is the coexistence of active and inactive (“dormant”) species, being in a dynamic equilibrium, either via *reversible deactivation* processes or via *reversible (degenerative) transfer*.

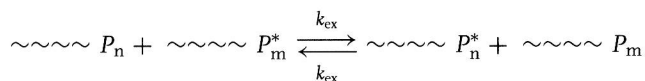
*Reversible deactivation* is a process where active species (ions, ion pairs, or radicals),  $P^*$ , are in a dynamic equilibrium with inactive (dormant), typically covalent species,  $P$ ,





Here,  $C$  is a catalyst (coinitiator/activator) and  $D$  is a deactivator or product of the activation process. As an example, in atom transfer radical polymerization (ATRP),  $P$  can be a bromine-terminated chain end,  $C$  can be a  $\text{Cu(I)}$  compound,  $P^*$  is the propagating radical, and  $D$  is a  $\text{Cu(II)}$  compound (Chapter 3). In GTP,  $P$  is a silylketene acetal,  $C$  can be a bifluoride anion,  $P^*$  can be an enolate, and  $D$  is a silyl fluoride (Chapter 1).

*Reversible transfer* is a bimolecular reaction between a dormant and an active polymer chain, which only differ in their degree of polymerization (degenerative transfer, i.e., equilibrium constant  $K_{\text{ex}} = 1$ ), leading to a direct exchange of activity between two chain ends:



A typical example is the exchange reaction between an iodine-terminated chain end and a propagating radical. Reversible addition–fragmentation chain transfer (RAFT) polymerization is also closely related to such a process (Chapter 3).

As a consequence of these processes, the MWD may be considerably broader than the Poisson distribution, where the polydispersity index,  $\text{PDI} = M_w/M_n$ , is close to unity. The PDI depends on the ratio of the rate constants of propagation to deactivation (or exchange) and decreases with monomer conversion [6]. If deactivation/exchange is slow relative to propagation, broad MWDs are observed. Many such systems have been called nonliving, because broad MWDs were assumed to originate in chain breaking reactions.

The first four chapters in this book present the mechanisms and the most recent advances in controlled/living polymerization of vinyl monomers. The first chapter summarizes anionic polymerization using classic systems and also recent developments employing equilibria between active and dormant species that enabled reduction of the rate of polymerization of styrene and also controlled polymerization of (meth)acrylates. The second chapter is devoted to carbocationic polymerization and illustrates examples of equilibria between carbocations and various dormant species and their applications to synthesis of well-defined (co)polymers. The third chapter describes a state of the art in controlled radical polymerizations, predominantly in stable free radical polymerization, atom transfer radical polymerization, and degenerative systems such as RAFT, and also presents how controlled molecular architecture can lead to new applications. The fourth chapter is focused on controlled/living coordination polymerization of olefins and presents some new materials prepared by this technique.

The next two chapters are focused on ring-opening polymerization. Chapter 5 presents recent advances in both anionic and cationic polymerization of heterocyclics together with examples of well-defined (co)polymers and their applications. Chapter 6 is focused on ROMP of cycloolefins and a variety of resulting new materials prepared by ROMP.



Chapters 7 and 8 illustrate how various controlled/living polymerizations can be employed to precisely control various elements of macromolecular architecture, such as chain composition and microstructure, chain topology and functionality, including block and graft copolymers. Chapter 9 presents how segmented copolymers self-organize in bulk, thin films, and solution into various nanostructured morphologies and how precise synthesis and processing can generate new materials with exciting properties.

Finally, the last chapter provides not only a state-of-the-art summary of current and forthcoming applications of Kraton, a large-volume block copolymer prepared by anionic vinyl polymerization, but also (co)polymers prepared by other controlled/living techniques.

We are confident that this book provides an excellent overview of various controlled/living polymerization techniques and hope that it will stimulate new discoveries and will facilitate developments of new polymeric materials for many exciting applications.

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*Axel H.E. Müller and Krzysztof Matyjaszewski*

## List of Contributors

**Volker Abetz**

Institute of Polymer Research  
GKSS Research Centre  
Geesthacht GmbH,  
Max-Planck-Str. 1  
21502 Geesthacht  
Germany

**Durairaj Baskaran**

University of Tennessee  
Department of Chemistry  
552 Buehler Hall, Knoxville  
TN 37996  
USA

**Christopher W. Bielawski**

The University of Texas at Austin,  
Department of Chemistry  
and Biochemistry, Austin  
TX 78712  
USA

**Andrew D. Bolig**

University of North Carolina at  
Chapel Hill  
Department of Chemistry, Chapel Hill  
NC 27599-3290  
USA

**Adriana Boschetti-de-Fierro**

Institute of Polymer Research  
GKSS Research Centre  
Geesthacht GmbH  
Max-Planck-Str. 1  
21502 Geesthacht  
Germany

**Maurice Brookhart**

University of North Carolina at  
Chapel Hill  
Department of Chemistry, Chapel Hill  
NC 27599-3290  
USA

**Geoffrey W. Coates**

University of North Carolina at  
Chapel Hill  
Department of Chemistry, Chapel Hill  
NC 27599-3290  
USA

**Marek Cypriak**

Centre of Molecular and Macromole-  
cular Studies  
Polish Academy of Sciences,  
Sienkiewicza 112  
PL-90-365 Lodz  
Poland

**Priyadarsi De**

University of Massachusetts Lowell  
Department of Chemistry  
One University Avenue, Lowell  
Massachusetts 01854  
USA

**Gregory J. Domski**

Cornell University, Department of  
Chemistry and Chemical Biology,  
Baker Laboratory, Ithaca  
New York 14853-1301  
USA

**Andrzej Duda**

Centre of Molecular and Macromolec-  
ular Studies  
Polish Academy of Sciences,  
Sienkiewicza 112  
PL-90-365 Lodz  
Poland

**Joseph B. Edson**

Cornell University  
Department of Chemistry and Chem-  
ical Biology, Baker Laboratory, Ithaca  
New York 14853-1301  
USA

**Rudolf Faust**

University of Massachusetts Lowell  
Department of Chemistry, One  
University Avenue, Lowell  
Massachusetts 01854  
USA

**Jean-François Gohy**

Université catholique de Louvain  
(UCL),  
Unité de Chimie des Matériaux  
Inorganiques et Organiques (CMAT),  
Place Pasteur 1  
1348 Louvain-la-Neuve  
Belgium  
&  
Eindhoven University of Technology  
Laboratory of Macromolecular  
Chemistry and Nanoscience,  
P.O. Box 513  
5600 MB Eindhoven  
The Netherlands

**Robert H. Grubbs**

Division of Chemistry and Chemical  
Engineering  
California Institute of Technology,  
Pasadena  
CA 91125  
USA

**Nikos Hadjichristidis**

University of Athens  
Department of Chemistry,  
Panepistimiopolis Zografou  
15771 Athens  
Greece

**Dale L. Handlin, Jr.**

PPG Fiber Glass  
940 Washburn Switch Road, Shelby  
NC 28150  
USA

**David R. Hansen**

SBC Polymers Consulting  
6330 FM 359 S, Fulshear  
TX 77441  
USA

**Hermis Iatrou**

University of Athens  
Department of Chemistry,  
Panepistimiopolis Zografou  
15771 Athens  
Greece

**Przemyslaw Kubisa**

Centre of Molecular  
and Macromolecular Studies  
Polish Academy of Sciences,  
Sienkiewicza 112  
PL-90-365 Lodz  
Poland

**Krzysztof Matyjaszewski**

Department of Chemistry  
Carnegie Mellon University  
4400 Fifth Avenue, Pittsburgh  
PA 15213-3890  
USA

**Axel H.E. Müller**

Universität Bayreuth  
Makromolekulare Chemie II  
95440 Bayreuth  
Germany

**Stanislaw Penczek**

Centre of Molecular  
and Macromolecular Studies  
Polish Academy of Sciences,  
Sienkiewicza 112  
PL-90-365 Lodz  
Poland

**Marinos Pitsikalis**

University of Athens  
Department of Chemistry  
Panepistimiopolis Zografou  
15771 Athens  
Greece

**Jeffrey M. Rose**

Cornell University  
Department of Chemistry  
and Chemical Biology,  
Baker Laboratory, Ithaca  
New York 14853-1301  
USA

**Georgios Sakellariou**

University of Athens  
Department of Chemistry  
Panepistimiopolis Zografou  
15771 Athens  
Greece

**Stanislaw Słomkowski**

Centre of Molecular  
and Macromolecular Studies  
Polish Academy of Sciences  
Sienkiewicza 112  
PL-90-365 Lodz  
Poland

**Scott R. Trenor**

Milliken Chemical  
920 Milliken Road  
M-401, Spartanburg  
SC 29303  
USA

**Constantinos Tsitsilianis**

University of Patras  
Department of Chemical Engineering  
FORTH/ICE-HT  
GR-26504 Patras  
Greece

**Kathryn J. Wright**

Kraton Polymers, 16, 400 Park Row  
Houston  
TX 77084  
USA

## Contents

**Preface** XV

**List of Contributors** 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

### 3 Radical Polymerization 103

*Krzysztof Matyjaszewski*

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