

Contents

Acknowledgements	iii
Abstract	viii
1 An Introduction to Functional Polymers and ROMP	1
1.1 Synthetic Polymer Basics	2
1.1.1 Synthesis	2
1.1.2 Characterization	3
1.2 Olefin Metathesis	4
1.2.1 Olefin Metathesis Catalysts	5
1.2.2 Ring-Opening Metathesis Polymerization	7
1.3 Objectives of this Work	10
References Cited	12
2 Polycyclooctatetraene (Polyacetylene) Produced with a Ruthenium Olefin Metathesis Catalyst	14
2.1 Abstract	15
2.2 Introduction	15
2.3 Results and Discussion	16
2.4 Experimental Section	20
References Cited	22
3 Direct Synthesis of Soluble, End-Functionalized Polyenes and Polyacetylene Block-Copolymers	23

3.1 Abstract	24
3.2 Introduction	24
3.3 Results and Discussion	27
3.3.1 Synthesis of Soluble Polyenes	27
3.3.1.1 Characterization of Soluble Polyenes	29
3.3.2 Synthesis of PA-containing Block Copolymers	33
3.3.2.1 Characterization of Block Copolymers	37
3.4 Conclusions	41
3.5 Experimental Section	42
3.6 Acknowledgement	45
References Cited	46
4 Formation of Covalently Attached Polymer Overlays on Si(111) Surfaces Using Ring-Opening Metathesis Polymerization Methods	49
4.1 Abstract	50
4.2 Introduction	50
4.3 Results and Discussion	51
4.4 Conclusions	56
References Cited	57
5 Synthesis of Polymer Dielectric Layers for Organic Thin-Film Transistors via Surface-Initiated Ring-Opening Metathesis Polymerization	60
5.1 Abstract	61
5.2 Introduction	61
5.3 Experimental Section	66
5.4 Acknowledgements	69
References Cited	70
6 Ring-Opening Metathesis Polymerization of Functionalized-Low-Strain Monomers with Ruthenium-Based Catalysts	72

6.1 Abstract	73
6.2 Introduction	73
6.3 Results and Discussion	74
6.3.1 ROMP of Unsubstituted Monomers	74
6.3.2 ROMP of Substituted Monomers	75
6.3.3 Model for Low-Strain ROMP	78
6.4 Conclusions	80
6.5 Experimental Section	81
6.6 Acknowledgements	84
References Cited	85
7 Synthesis of Well-Defined Poly(vinylalcohol₂-<i>alt</i>-methylene) via Ring-Opening Metathesis Polymerization	87
7.1 Abstract	88
7.2 Introduction	88
7.3 Results and Discussion	91
7.3.1 Monomer Design and Synthesis	91
7.3.2 ROMP of Bicyclic Silicon-Protected Diol with 1	91
7.3.3 ROMP of Bicyclic Silicon-Protected Diol with 2 and a Chain Transfer Agent	93
7.3.4 Hydrogenation of Polymers	94
7.3.5 Deprotection of Polymers	97
7.3.6 Thermal Analysis	100
7.4 Conclusions	100
7.5 Experimental Section	102
7.6 Acknowledgment	104
References Cited	105
8 Synthesis and Characterization of Stereoregular Ethylene-Vinyl Alcohol Copolymers Made by Ring-Opening Metathesis	

Polymerization	107
8.1 Abstract	108
8.2 Introduction	108
8.3 Results and Discussion	111
8.3.1 Monomer Design and Synthesis	111
8.3.2 ROMP of Acetonide Monomers with Catalyst 1	112
8.3.3 ROMP of Acetonide Monomers with Catalyst 2	114
8.3.4 Hydrogenation of Acetonide-Protected ROMP Polymers . . .	116
8.3.5 Deprotection of Acetonide Groups	117
8.3.6 Thermal Analysis of ROMP, Hydrogenated, and Deprotected Polymers	118
8.4 Conclusions	119
8.5 Experimental Section	120
8.6 Acknowledgements	123
References Cited	124
9 Computational Study on the Effect of Controlled Stereochemistry on Oxygen Permeability in EVOH Materials	126
9.1 Abstract	127
9.2 Introduction	127
9.3 Simulation Methods	128
9.4 Results and Discussion	130
9.4.1 Hydrogen Bond Analysis	130
9.4.2 Free Volume Analysis	133
9.4.3 Oxygen Diffusivity	136
9.5 Conclusions	138
References Cited	139

List of Figures

1.1	Olefin metathesis	5
1.2	Chemical transformations by olefin metathesis	5
1.3	Reactivity of olefin metathesis catalysts	6
1.4	Recent advances in ruthenium catalysts	7
1.5	ROMP of a cyclic olefin	7
1.6	Representative monomers and strain energies	8
2.1	Several olefin metathesis active catalysts	16
2.2	ROMP of COT and four isomeric microstructures of PA	17
2.3	Solid-state ^{13}C NMR of poly(COT)	18
2.4	SEM of poly(COT)	20
3.1	Ruthenium olefin metathesis catalysts	26
3.2	Chain transfer agents	28
3.3	^1H NMR spectrum of telechelic polyene	31
3.4	UV-Vis spectrum of telechelic polyene	32
3.5	FT-IR of telechelic polyenes	32
3.6	MALDI-TOF MS spectrum of telechelic polyene	33
3.7	Olefin-terminated polymers	35
3.8	UV-vis spectra of PA-containing block copolymers in CH_2Cl_2 solution .	38
3.9	FT-IR spectra PA- <i>b</i> -PMMA block copolymer and PMMA	39
3.10	Tapping Mode AFM images	41
4.1	XPS survey scans	53
4.2	SEM of polynorbornene-modified Si(111) surface	54

5.1	Catalysts and linkers for SI-ROMP	62
5.2	Current-voltage characteristics of an FET produced by lamination	64
5.3	Current-voltage characteristics of an FET produced by direct deposition	65
6.1	Ruthenium olefin metathesis catlayssts	74
6.2	Isodesmic reaction	79
6.3	Correlation between calculated and experimental strain energies	80
7.1	Ruthenium olefin metathesis catalysts	89
7.2	ROMP of a symmetric bicyclic monomer with a ruthenium catalyst . .	92
7.3	Graphs of molecular weight control for ROMP of with a ruthenium catalyst	92
7.4	ROMP of a symmetric bicyclic monomer in the presence of a CTA with a ruthenium catalyst	94
7.5	^1H and ^{13}C NMR spectrum of MVOH ROMP polymer	96
7.6	Structures of the <i>m</i> and <i>r</i> dyads in MVOH	97
7.7	^1H and ^{13}C NMR spectrum of deprotected MVOH polymer	99
7.8	DSC and TGA analysis of MVOH	101
8.1	Metathesis-based routes to EVOH copolymers	109
8.2	Ruthenium olefin metathesis catalysts	110
8.3	Graphs of MW control and yields from ROMP of <i>trans</i> -acetonide-monomer	113
8.4	Plot of MW control from ROMP of <i>cis</i> -acetonide-monomer	114
8.5	Plot of MW control from ROMP of <i>cis</i> -acetonide-monomer with a chain transfer agent	116
9.1	Mean square displacement of polymer atoms at 300 K	130
9.2	Types of intra-chain hydrogen bonding	131
9.3	Extended hydrogen bonding in EVOH materials	132
9.4	Probability of hydrogen bond cluster sizes	133
9.5	Comparison of void spaces in syn and anti EVOH copolymers	134
9.6	Comparison of void spaces in EVOH copolymers	135
9.7	Time evolution of the free volume for EVOH copolymer 5	136

9.8	Time evolution of the free volume for EVOH copolymer 6	137
9.9	Average displacement of atoms in polymer and O ₂ in molecular dynamics run	137

List of Schemes

1.1	Telechelic polymer formation by ROMP with a CTA	8
1.2	Mechanism for the synthesis of telechelic polymers by ROMP	9
4.1	Si(111) surface modification procedure	52
5.1	Construction of an FET using a SI-ROMP polymer dielectric layer . .	63
6.1	ROMP of cyclopentene and cycloheptene	75
6.2	ROMP of substituted low-strain monomers	77
7.1	Attempt to ROMP cyclopentene monomers	90
7.2	A bicyclic protection strategy	90
7.3	Synthetic route to MVOH	91
8.1	ROMP of cyclooctene- <i>trans</i> -diol	110
8.2	Protection strategies for <i>trans</i> and <i>cis</i> cyclooctene-diol monomers .	112
8.3	ROMP of <i>trans</i> -acetonide-protected diol	112
8.4	ROMP of <i>cis</i> -acetonide-protected diol	114
8.5	ROMP of <i>cis</i> -acetonide-protected diol with a chain transfer agent .	115
8.6	Hydrogenation of acetonide-protected polymers	117
8.7	Deprotection of acetonides	118
9.1	General synthetic route to EVOH materials	128

List of Tables

2.1	Comparison of polyacetylenes	17
3.1	Polyene yields vs monomer/CTA and monomer/catalyst ratios	28
3.2	Variation in composition of PA block copolymers.	36
4.1	Dependence of polymer film thickness on monomer concentration . . .	55
6.1	Results for the ROMP of cyclopentene and cycloheptene with ruthenium catalysts at 25 °C	76
6.2	Results for the ROMP of substituted cyclopentenes and cycloheptenes with ruthenium catalysts at 25 °C	78
6.3	Calculated strain energies and “ROMP-ability” for several low-strain monomers.	80
7.1	ROMP of a symmetric bicyclic monomer with a ruthenium catalyst . .	93
7.2	ROMP of a symmetric bicyclic monomer in the presence of a CTA with a ruthenium catalyst	94
8.1	ROMP of a <i>cis</i> -acetonide cyclooctene monomer with a ruthenium catalyst	115
8.2	ROMP of a <i>cis</i> -acetonide cyclooctene monomer in the presence of a CTA with a ruthenium catalyst	117
8.3	Thermal analysis of ROMP, hydrogenated, and deprotected EVOH polymers	118