

## **Abstract**

SETO, KEITARO. Metal Catalyzed Polymerization of Cyclic Olefins. (Under the direction of Bruce M. Novak.)

We have been interested in polymerization of cyclic olefins using transition metal catalysts. Two important polymerization mechanisms have been studied, ring opening metathesis polymerization (ROMP) and coordination insertion polymerization.

Various kinds of transition metal complex are known to catalyze the ring opening metathesis polymerization. Among those transition metal complexes, ruthenium has a great advantage of decreased oxophilicity. The lower oxophilic nature of ruthenium allows to polymerize functionalized monomer and to utilize alcohol/water as reaction medium. Several examples of the polymerization of functionalized monomers are known, however, very few examples of the polymerization in water are known. In addition, ROMP does not involve extra reagents and production of byproducts. From a green chemistry standpoint, the utilization of water as solvent and clean reaction has a significance. We have reported the investigation of the ROMP of oxo-functionalized cyclic olefins in water using a ruthenium salt (Chapter 2).

The polynorbornene from the coordination-insertion polymerization has great features as engineering plastics, and because of its properties many research projects of the coordination polymerization of norbornene have been done. Whereas, few examples of polymerization studies of other cyclic olefin have been reported. Among these cyclic olefins, cyclobutene derivatives have never been reported because of side reactions, the facile

pericyclic ring opening reaction of cyclobutene during polymerization and ROMP. This is the first report that cyclobutene derivatives have been polymerized without such side reactions to afford high molecular weight addition polymer (Chapter 3).

# **Metal Catalyzed Polymerization of Cyclic Olefins**

by  
**Keitaro Seto**

A dissertation submitted to the Graduate Faculty of  
North Carolina State University  
in partial fulfillment of the  
requirement for the Degree of  
Doctor of Philosophy

**Chemistry**

Raleigh  
2006

**Approved By:**

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Bruce M. Novak, Chairman

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Jonathan S. Lindsey

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David A. Shultz

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Dimitris S. Argyropoulos

To the memory of my beloved mother

## **Biography**

The author was born on November 11, 1969 in Kanagawa, Japan. He joined textile company Unitika Ltd. after his completion of Master of Science, in the field of synthetic organic chemistry, under the direction of Prof. Mukaiyama at Science University of Tokyo. While he was working in Unitika Ltd. R & D center, he had a chance to study polymer chemistry at North Carolina State University under the supervision of Prof. Bruce M. Novak as visiting scientist for two years. This experience stimulated him to further study polymer chemistry. In 2003, he began his graduate education at North Carolina State University under the direction of Prof. Bruce M. Novak.

## **Acknowledgements**

I would like to thank my wife, Yuriko, and my son, Kanta, whose smiles have always provided encouragement. I also thank my father, Yoshimasa, and my sister, Chiharu for their support. My deepest appreciation goes to my deceased mother, Yoko who had always cheered me up. I could have never done what I have done in my life without her.

I would like to thank my advisor Prof. Bruce M. Novak for guidance and financial support during my graduate studies. Without him, I would have never imagined to study polymer chemistry in the graduate school. He provided excellent environment to study polymer chemistry in physically and mentally.

I also thank Dr. Ed Bowden, who helped with administrative matters. Thanks also go out to people who helped with things in and outside the lab, Crissy Williams-Brown, Teresa Henline, Jan Singhass, Cynthia Wertz, Maria Moreno and Brenda Burgess.

## Table of Contents

List of Figures .....	viii
List of Tables .....	xii
List of Schemes .....	xiii
Chapter 1: Introduction to Olefin Polymers.....	1
1.1 Introduction.....	1
1.2 Several Types of Olefin Polymer.....	3
1.2.1 Polyethylene and Polypropylene .....	3
1.2.2 Polynorbornene.....	6
1.3 Cyclic Olefins .....	8
1.4 References and Notes.....	10
Chapter 2: Ring Opening Metathesis Polymerization (ROMP) in Water.....	12
2.1 Introduction to ROMP .....	12
2.1.1 Brief History of ROMP .....	12
2.1.2 The Classification of ROMP Catalyst .....	19
2.2 Target Polymerization.....	24
2.2.1 Green Chemistry.....	24
2.2.2 Olefin Metathesis Ruthenium Catalyst (Background) .....	25
2.2.3 New Monomer.....	29
2.2.4 Problem and Objective .....	32
2.3 Preparation of monomer .....	32
2.3.1 Diels-Alder reaction .....	32

2.3.2 Stereo Selectivity .....	35
2.4 Polymerization Study .....	37
2.4.1 Comparison of Commercially Available $K_2RuCl_5 \cdot H_2O$ .....	37
2.4.2 Polymerization Activity .....	38
2.5 Revealment of the Real Catalyst precursor .....	40
2.5.1 Thermal Analysis of $K_2RuCl_5 \cdot H_2O$ .....	40
2.5.2 UV-Vis Analysis and pH Analysis of solution .....	41
2.5.3 X-ray Powder Diffraction .....	42
2.5.4 Synthesis of $K_2RuCl_5 \cdot H_2O$ .....	44
2.6 Conclusion .....	44
2.7 Experimental Section .....	46
2.7.1 General Procedures and Characterization .....	46
2.7.2 Procedures .....	46
2.8 References and Notes .....	48
Chapter 3: Polymerization of Cyclobutene Derivatives .....	53
3.1 Introduction of Coordination-Insertion Polymerization Catalyst .....	53
3.2 Coordination-Insertion Polymerization of Cyclobutene .....	68
3.2.1 Polymerization of 1,2-Disubstituted Olefin .....	68
3.2.2 Polymerization of Cyclic Olefin .....	70
3.2.3 Cyclobutene Polymerization .....	76
3.2.4 New Monomer .....	77
3.3 Ring Strain .....	80

3.3.1 Evaluation of Ring Strain (Calculation Method).....	80
3.3.2 Ring Strain of New Monomers (Comparison with Norbornene) .....	83
3.4 Preparation of New Monomers.....	84
3.5 Polymerization Studies .....	86
3.5.1 Choice of Catalyst Systems .....	86
3.5.2 Result from Preliminary Polymerization Studies .....	89
3.5.3 Origin of Olefin Structure .....	90
3.5.4 New Zirconium Catalyst.....	102
3.5.5 Chain Transfer Reaction (co-catalyst study) .....	110
3.6 Characterization of The Polymers .....	114
3.6.1 Thermal Analysis.....	114
3.6.2 X-ray Powder Diffraction Analysis .....	119
3.7 Conclusion .....	124
3.8 Experimental Section.....	126
3.8.1 General Procedures and Characterization .....	126
3.8.2 Procedures .....	127
3.8.3 NMR Spectra (Selected Samples) .....	137
3.9 References and Notes.....	142

## List of Figures

<b>Figure 1.1:</b> Schematic representation of the different classes of polyethylene. (a) high density polyethylene; (b) low density polyethylene; (c) linear low density polyethylene. ....	4
<b>Figure 1.2:</b> Two possible chiral coordinations of propylene to a metal center.....	5
<b>Figure 1.3:</b> Mechanism of ROMP (norbornene is shown as monomer).....	7
<b>Figure 1.4:</b> Pericyclic reactions a) Diels-Alder reaction between cyclopentadiene and ethylene b) Dimerization of cyclopentadiene c) 1,3-cycloheptadiene to bicyclo[3.2.0]-hept-6-ene d) 1,3-cyclooctadiene to bicyclo[4.2.0]oct-7-ene e) Diels-Alder reaction with functional group.....	9
<b>Figure 2.1:</b> Proposed mechanism by Chauvin. (Reproduced from <i>Die Makromolekulare Chemie</i> <b>1970</b> , 141, 161).....	17
<b>Figure 2.2:</b> Early example of well-defined catalysts a) Schrock type b) Grubbs type .....	18
<b>Figure 2.3:</b> Metal halide-metal alkyl olefin metathesis catalyst systems. ....	20
<b>Figure 2.4:</b> Carbene Ligand Transition Metal Olefin Metathesis Catalyst.....	21
<b>Figure 2.5:</b> Catalysts with no alkyl agent and preformed carbene.....	23
<b>Figure 2.6:</b> Water-Soluble ruthenium carbene complex for olefin metathesis reactions.....	25
<b>Figure 2.7:</b> Ion binding cavity formed from a helical turn of poly(7-oxonorbornene).....	28
<b>Figure 2.8:</b> Steric repulsion in polymers obtained from <i>endo</i> and <i>exo</i> isomers of dicyclopentadiene. ....	36
<b>Figure 2.9:</b> Thermogravimetric analysis of the four “K <sub>2</sub> RuCl <sub>5</sub> ” samples.....	40
<b>Figure 2.10:</b> UV analysis (10 <sup>-6</sup> M in 10 mL of 12 M HCl).....	41
<b>Figure 2.11:</b> X-ray powder diffraction pattern of three “K <sub>2</sub> RuCl <sub>5</sub> ” samples.....	43
<b>Figure 3.1:</b> Schematic presentation of olefin coordination to transition metal (Dewar-Chatt-Duncanson model) .....	54

<b>Figure 3.2:</b> Examples of metallocene catalysts.....	56
<b>Figure 3.3:</b> Relation between metallocene symmetry and tacticity .....	58
<b>Figure 3.4:</b> Optimized geometries of (A) $\text{Cp}_2\text{ZrCH}_3^+$ , <b>I</b> and (B) $\text{SiH}_2\text{Cp}_2\text{ZrCH}_3^+$ , <b>II</b> . (Reproduction from <i>Organometallics</i> <b>1994</b> , 13, 2252).....	59
<b>Figure 3.5:</b> General structure of constrained geometry complex (cationic) and optimized geometry, where $\text{M}=\text{Zr}$ , $\text{R}=\text{R}'=\text{H}$ . (Reproduction from <i>Organometallics</i> <b>1994</b> , 13, 2252) .....	60
<b>Figure 3.6:</b> Mitsui Chemicals catalysts; (A) phenoxy-imine ( $\text{R}_1, \text{R}_2$ is alkyl group. $\text{R}_3$ is phenyl group. $\text{M}$ is Ti, Zr or Hf.) (B) pyrrolide-imine ( $\text{R}$ is alkyl or phenyl group. $\text{M}$ is Zr or Ti.).....	62
<b>Figure 3.7:</b> General structure of Brookhart nickel and palladium catalysts. ( $\text{M}=\text{Ni}$ or $\text{Pd}$ , $\text{X}=\text{alkyl}$ or halogen, $\text{R}$ and $\text{R}'=\text{alkyl}$ ) .....	63
<b>Figure 3.8:</b> Steric interactions between bulky aryl ligands and axial coordination site of the metal center. ....	64
<b>Figure 3.9:</b> Optimized structures of resting state, (A) and transition state of termination, (B). Propyl metal cation and ethylene are used as model. (Reproduced from <i>J. Am. Chem. Soc.</i> <b>1997</b> , 119, 6177).....	64
<b>Figure 3.10:</b> Brookhart and Gibson iron catalyst for ethylene and $\alpha$ -olefin polymerization.	65
<b>Figure 3.11:</b> Grubbs “neutral” nickel catalyst. ....	66
<b>Figure 3.12:</b> Copolymerization neutral nickel catalyst for ethylene and methyl methacrylate. ....	67
<b>Figure 3.13:</b> Stereochemical orientations and numbering in a norbornene. ....	73
<b>Figure 3.14:</b> Simple nickel complex catalyzed norbornene polymerization. <sup>86,90</sup> .....	74
<b>Figure 3.15:</b> Fused ring cyclobutene monomers.....	77
<b>Figure 3.16:</b> Thermally allowed conrotatory orbital correlation diagram. ....	79
<b>Figure 3.17:</b> Catalyst systems for preliminary polymerization studies. ....	88
<b>Figure 3.18:</b> NMR spectra of (a) poly-romp- <b>3</b> in $\text{CDCl}_3$ and (b) polymer sample from reaction <b>3</b> with $\text{CpZrCl}_3$ in $\text{CDCl}_3$ .....	92

<b>Figure 3.19:</b> Optimal conformation of monomer <b>3</b> .....	94
<b>Figure 3.20:</b> Schematic representation of metal- $\beta$ -hydrogen overlap. ....	94
<b>Figure 3.21:</b> Predicted $^{13}\text{C}$ chemical shifts of <b>poly-3</b> with terminal olefin.....	96
<b>Figure 3.22:</b> Short range $^1\text{H}$ - $^{13}\text{C}$ correlation NMR spectrum of polymeric sample from monomer <b>3</b> with $\text{CpZrCl}_3$ in toluene- $\text{d}_8$ . ....	97
<b>Figure 3.23:</b> Long range $^1\text{H}$ - $^{13}\text{C}$ correlation NMR spectrum of polymeric sample from monomer <b>3</b> with $\text{CpZrCl}_3$ in toluene- $\text{d}_8$ .....	98
<b>Figure 3.24:</b> Chemical shift of $\beta$ -agostic complex at $-110 \sim -130^\circ\text{C}$ in $\text{CDCl}_2\text{F}$ . <sup>116-118</sup> .....	100
<b>Figure 3.25:</b> Five possible isomers for Mitsui catalyst.....	103
<b>Figure 3.26:</b> $^1\text{H}$ -NMR spectra of polymeric product from monomer <b>3</b> (a) catalyzed by $\text{CpZrCl}_3$ and (b) catalyzed by Mitsui Zr, in o-DCB- $\text{d}_4$ at room temperature. .	106
<b>Figure 3.27:</b> $^{13}\text{C}$ -NMR spectra of (a) monomer <b>3</b> homopolymer and (b) ethylene monomer <b>3</b> copolymer at $130^\circ\text{C}$ in o-DCB- $\text{d}_4$ .....	108
<b>Figure 3.28:</b> GPC comparison of homopolymer and copolymer.....	109
<b>Figure 3.29:</b> DSC analysis of selected samples and low molecular weight <b>poly-3</b> ( $M_w = 3,300$ ).....	115
<b>Figure 3.30:</b> DSC analysis of low molecular weight <b>poly-3</b> ( $M_w = 3,300$ ) and <b>poly-4</b> (unknown $M_w$ due to insolubility) at slower rate of temperature ( $5^\circ\text{C}/\text{min}$ ). .	116
<b>Figure 3.31:</b> DSC analysis comparison of various molecular weight samples of <b>poly-3</b> ....	117
<b>Figure 3.32:</b> The comparison of DSC curves of three polymers, <b>poly-3</b> , <b>poly-4</b> , and polynorbornene.....	118
<b>Figure 3.33:</b> WAXD diagram of polynorbornene. (Reproduction from <i>Macromol. Chem. Phys.</i> <b>1996</b> 197 3435) .....	120
<b>Figure 3.34:</b> X-ray powder diffraction diagram of polynorbornene catalyzed by $\text{Ni}(\text{acac})_2$ . ....	121
<b>Figure 3.35:</b> X-ray powder diffraction diagram of <b>poly-3</b> ( $M_w = 220,000$ ). ....	122

<b>Figure 3.36:</b> Solid state NMR spectra of (a) <b>poly-3</b> and (b) <b>poly-4</b> . .....	137
<b>Figure 3.37:</b> Estimated $^{13}\text{C}$ chemical shift of <b>ethylene-3-copolymer</b> and <b>poly-3</b> . .....	138
<b>Figure 3.38:</b> $^{13}\text{C}$ -NMR spectrum of <b>poly-3</b> in <i>o</i> -DCB- $\text{d}_4$ at $130^\circ$ .....	138
<b>Figure 3.39:</b> $^{13}\text{C}$ -NMR spectrum of <b>poly-3</b> in <i>o</i> -DCB- $\text{d}_4$ at $130^\circ$ .....	139
<b>Figure 3.40:</b> DEPT spectrum of <b>poly-3</b> . .....	139
<b>Figure 3.41:</b> $^{13}\text{C}$ -NMR spectrum of <b>ethylene-3-copolymer</b> in <i>o</i> -DCB- $\text{d}_4$ at $130^\circ$ . .....	140
<b>Figure 3.42:</b> $^{13}\text{C}$ -NMR spectrum of <b>ethylene-3-copolymer</b> in <i>o</i> -DCB- $\text{d}_4$ at $130^\circ$ . .....	141
<b>Figure 3.43:</b> DEPT spectrum of <b>ethylene-3-copolymer</b> . .....	141

## List of Tables

<b>Table 2.1:</b> Functional group tolerance of transition metal olefin metathesis catalysts .....	27
<b>Table 2.2:</b> Ruthenium complex; Color of four different brands .....	37
<b>Table 2.3:</b> Polymerization result .....	38
<b>Table 2.4:</b> Elemental analysis of two “K <sub>2</sub> RuCl <sub>5</sub> ” samples. ....	39
<b>Table 2.5:</b> pH of aqueous solutions of the four samples of “K <sub>2</sub> RuCl <sub>5</sub> •nH <sub>2</sub> O”. ....	42
<b>Table 3.1:</b> Strain energies based on experimentally determined heats of formation. <sup>67</sup> .....	80
<b>Table 3.2:</b> Heats of formation of small molecules. <sup>99</sup> .....	82
<b>Table 3.3:</b> Polymerization Results of monomer <b>3</b> with various catalyst systems.....	89
<b>Table 3.4:</b> Strain energies of bridgehead olefins calculated by Maier <i>et al.</i> <sup>100</sup> .....	95
<b>Table 3.5:</b> Monomer <b>3</b> polymerization with Mitsui Zr with MAO.....	105
<b>Table 3.6:</b> Molecular weight of selected samples. ....	109
<b>Table 3.7:</b> Results of activator modification to polymerize monomer <b>3</b> . ....	114
<b>Table 3.8:</b> The short-order distance derived from halos using Eq. (7). ....	121

## List of Schemes

<b>Scheme 1.1:</b> Two possible monomer insertion.....	5
<b>Scheme 2.1:</b> Three types of Olefin metathesis reaction .....	12
<b>Scheme 2.2:</b> Early examples of olefin metathesis reactions .....	13
<b>Scheme 2.3:</b> Polymerization pathway proposed by Truett. ....	14
<b>Scheme 2.4:</b> The confirmation of double bond cleavage-recombination.....	14
<b>Scheme 2.5:</b> Another evidence of double bond cleavage.....	15
<b>Scheme 2.6:</b> “pair-wise” mechanism .....	15
<b>Scheme 2.7:</b> An evidence for metal carabene mechanism. Cross-metathesis reaction, scrambling olefin components.....	16
<b>Scheme 2.8:</b> First living ROMP example.....	17
<b>Scheme 2.9:</b> First direct detection of metallacyclobutene complex during norbornene polymerization. ....	19
<b>Scheme 2.10:</b> ROMP of 7-oxonorbornene derivatives in water catalyzed by simple ruthenium salt. ....	27
<b>Scheme 2.11:</b> Synthetic route to monomer <b>1</b> from furan and maleic anhydride.....	29
<b>Scheme 2.12:</b> Copolymerizatoin of maleic anhydride / divinyl ether .....	31
<b>Scheme 2.13:</b> ROMP of monomer <b>2</b> in water catalyzed by $K_2RuCl_5$ .....	32
<b>Scheme 2.14:</b> Diels-Alder reaction; endo, exo selectivity in the case of maleic anhydride and cyclopentadiene.....	34
<b>Scheme 2.15:</b> Preparation of monomer <b>2</b> .....	35
<b>Scheme 2.16:</b> Synthesis of “aquochlororuthenate” .....	44
<b>Scheme 3.1:</b> Mechanism of “Coordination-Insertion Polymerization”. ....	53

<b>Scheme 3.2:</b> Diamide chelating Ti catalyst for $\alpha$ -olefin polymerization. <sup>25</sup> .....	61
<b>Scheme 3.3:</b> Proposed mechanism for trans-2-butene polymerization by Brookhart.....	69
<b>Scheme 3.4:</b> Coordination-Insertion polymerization of cyclopropene derivatives. ....	71
<b>Scheme 3.5:</b> 1,3-Enchainment of polycyclopentene .....	71
<b>Scheme 3.6:</b> Different types of polynorbornene. ....	72
<b>Scheme 3.7:</b> Living polymerization of norbornene and its oxy-functionalized derivative by palladium initiator. <sup>91</sup> .....	75
<b>Scheme 3.8:</b> Pericyclic ring opening reaction of butadiene. ....	76
<b>Scheme 3.9:</b> Polymer has very low molecular weight and ROMP structure. ....	77
<b>Scheme 3.10:</b> Our new monomers. ....	79
<b>Scheme 3.11:</b> Synthesis of monomer <b>3</b> from 1,5-cyclooctadiene. ....	84
<b>Scheme 3.12:</b> Synthesis of monomer <b>4</b> from 1,3-cycloheptadiene. ....	85
<b>Scheme 3.13:</b> Transformation of 1,3-cyclooctadiene compounds to cyclobutene. ....	85
<b>Scheme 3.14:</b> ROMP of monomer <b>3</b> . ....	91
<b>Scheme 3.15:</b> Polymerization of monomer <b>4</b> by Ni(acac) <sub>2</sub> and B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> .....	99
<b>Scheme 3.16:</b> Formation of $\beta$ -agostic complex from monomer <b>4</b> .....	100
<b>Scheme 3.17:</b> Synthesis of $\beta$ -agostic complex from monomer <b>4</b> .....	101
<b>Scheme 3.18:</b> Synthesis of phenoxyimine.....	104
<b>Scheme 3.19:</b> Synthesis of zirconium complex .....	104

## **Chapter 1: Introduction to Olefin Polymers**

### **1.1 Introduction**

Since days immemorial, humans have utilized “polymer materials”; those natural occurring polymers are such as shellac, amber and latex. Very late in human history, in the middle of 18<sup>th</sup> century, we have begun to modify those natural polymers by modern chemical techniques. The inventions include some famous and still useful materials like, vulcanized rubber and celluloid. It took us another hundred years to create the first genuine synthetic polymer, Bakelite, which was in 1909. Then soon after, the first synthetic fiber Nylon was introduced to commodity market in 1911.<sup>1</sup> Gibson et al. filed an industrial polyethylene production process in late 1930s.<sup>2</sup> It has been less than a century since the introduction of the first synthetic polymers to our daily life, and today we are surrounded number of polymer products. Even though polymer materials are fairly new and have simple chemical formula, our life depends on polymer material in many aspects.

According to “American Plastics Council”, in 2004 the production of thermosets and thermoplastics polymers in the United States and other North American countries is increased by little more than 8% from year 2003, and number reached 115 billion pounds. The production of polyolefins, such as polyethylene, polypropylene, and polystyrene, is nearly 80 billion pounds, 70% of total polymer production. From these numbers, we literally rely on polyolefins from economics to daily life. Given these numbers, it is quite surprising that it has been only 70 years since Staudinger revealed the true nature of polymeric materials.

Creating a new class of polymers draws intensive new interest. Because synthetic polymers are relatively new materials, we have plenty of untouched places to explore for new materials. There are many possibilities to improve the properties of existing polymer materials or develop new ones. This is indeed a challenging task, but there should be a lot of ideas or ways that we can imagine and try, for example, developing a new monomer, developing a new polymerization technique, modifying the existing polymers, and even combining two or more techniques.

Most of the polyolefins that are produced these days are made from ethylene, propylene and styrene as monomers. Those monomers are readily available from petroleum oil in relatively inexpensive (at least for now). For such mass-produced and mass-consumed polymers, monomer preparation is also important in the polymerization process. Simple and less synthetic intense procedures are required. Taking into account these, it is understandable that ethylene, propylene and styrene have the major role in polyolefin industry. Nevertheless, there is the possibility of developing new olefin polymers by employing other simple and inexpensive olefin monomers.

Meanwhile, considering of natural environment, we seek for the processes that are environmentally conscious. In other words, the green chemistry offers a low load to natural environment and use recyclable materials.

In summary, developing new routes to unusual materials are important themes in today's world which include green chemistry, synthesis of polymer with well-defined structures, and polymers with high performance properties. We have looked at projects in all these areas:

1. Aqueous Ring Opening Metathesis Polymerization (ROMP) by  $\text{Ru}^{3+}$  complex
2. Polymerization of cyclobutene derivatives

In the following chapters include results and discussion for these two projects.

## **1.2 Several Types of Olefin Polymer**

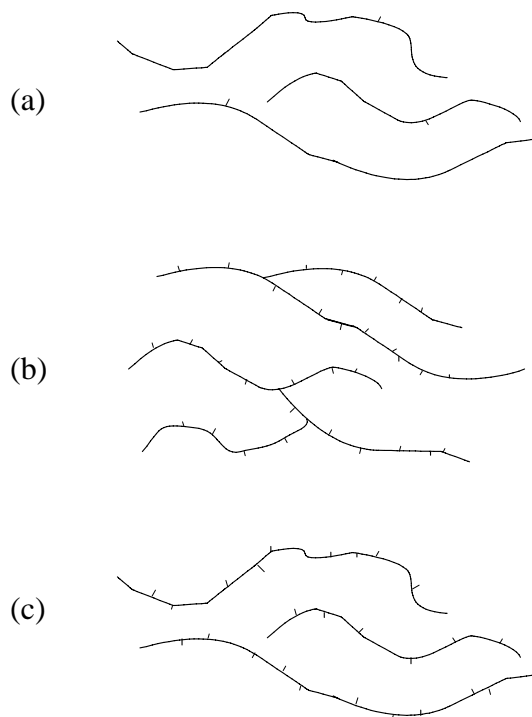
### ***1.2.1 Polyethylene and Polypropylene***

In 2004, about 40 billion pounds of polyethylene was produced, which is close to 35% of the total polymer production in the United States.<sup>1</sup> Among polyolefins, the most popular material in today's world is polyethylene. It generally can be classified into three different types of polyethylene based on its microstructure, Figure 1.1. Those differences in microstructure originate from its polymerization process.

High-pressure (ranging from 14,000 to 56,000 psi) radical process is employed to produce low-density polyethylene, Figure 1.1 (b). Because of random reactivity of radicals, this polymerization process produces long branched chain.<sup>3,4</sup> These long branches make this polyethylene have a relatively low density, and low crystallinity.

On the other hand, high-density polyethylene and linear low-density polyethylene are produced from low-medium pressure (ranging from 20 to 1000 psi) metal catalyzed process. As a typical catalyst, Phillips catalyst and Ziegler-Natta catalyst can be listed. The former one is sometimes referred as metal-oxide catalyst and it was invented in 1950. Then in 1953, the latter catalyst was invented. Essentially, this process produces only high-density polyethylene, however when  $\alpha$ -olefin is introduced into polymerization process linear low-

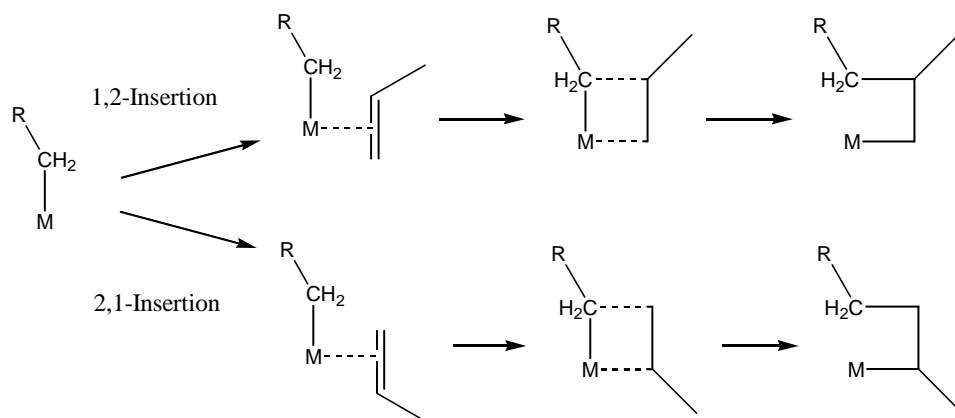
density polyethylene is produced.<sup>4</sup> Appearance of the Ziegler-Natta catalysts and next generation metal catalyst had a big impact on a development of new polymers.



**Figure 1.1:** Schematic representation of the different classes of polyethylene. (a) high density polyethylene; (b) low density polyethylene; (c) linear low density polyethylene.

Industrial production of isotactic polypropylene started in 1957 in Italy, 3 years later since discovery of isotactic propylene polymerization by Ziegler-Natta heterogeneous catalyst. One would realize from its structure that there are two selectivity problems in propylene polymerization, regioselectivity and stereoselectivity,<sup>3,5</sup> Scheme 1.1 and Figure 1.2.

**Scheme 1.1:** Two possible monomer insertion.



**Figure 1.2:** Two possible chiral coordinations of propylene to a metal center.

According to the considered mechanisms, isotactic polypropylene is formed from a long consecutive series of all *re* or all *si* coordinations and syndiotactic polypropylene is formed from alternate insertions of *re* and *si* coordinations. Regioselectivity also affects microstructure of polypropylene in different way that cause defect of bonding fashion “head-head” or “tail-tail”. Ziegler-Natta catalyst system is known as highly 1,2-insertion selective and isotactic selective.<sup>5</sup>

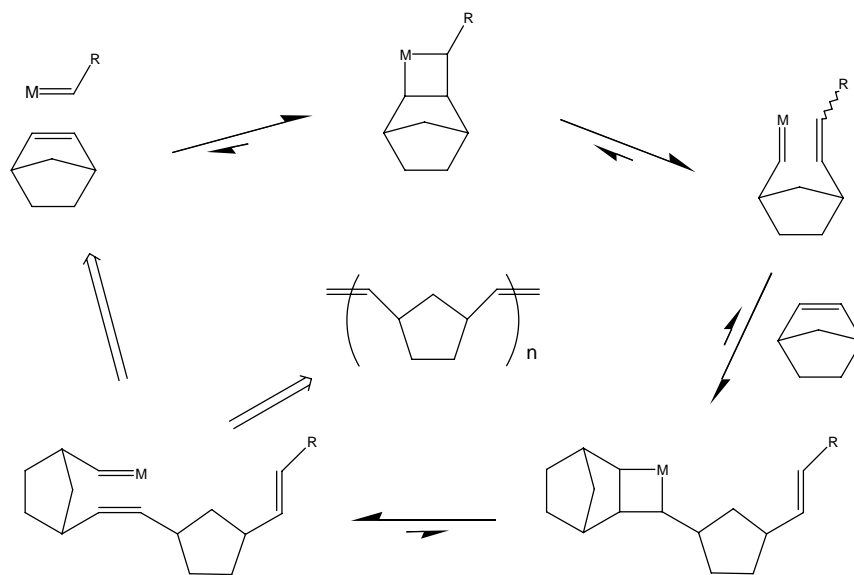
Since discovery of Ziegler-Natta heterogeneous catalyst systems, technologies of ethylene/propylene polymerization have advanced and still are advancing. Then development

of Kaminsky-Sinn homogeneous catalyst widened potential of olefin polymerization.<sup>6</sup> However, catalyst systems have far advanced since the early days, but still only simple linear olefins, ethylene and propylene, are utilized.

### ***1.2.2 Polynorbornene***

“Olefin polymer”, these words used to clearly mean addition polyolefin, such as polyethylene, until concept of “Olefin Metathesis Polymerization” was introduced. The expression “Olefin Metathesis” was first used in 1967.<sup>7</sup> The reaction was observed in 1950s, however it wasn’t until 1971 that a convincing mechanism was proposed.<sup>8,9</sup> Figure 1.3 shows the essential mechanism of Ring Opening Metathesis Polymerization (ROMP). During the polymerization cycle, first metal carbene complex forms a metallacyclobutene ring, then this cleaves to form a new carbene complex, this new carbene complex repeats these steps to afford a polymeric structure. As shown in Figure 1.3, this is a reversible reaction and a driving force is required toward polymer formation.

Norbornene, or bicyclo[2.2.1]-2-heptene, may be the most popular monomer for ROMP. In addition to that, norbornene also can be addition polymerized by radical, by cationic and most importantly by using highly sophisticated coordination-insertion catalyst systems.<sup>10,11</sup> Radical and cationic reactions are almost ignored since they yield only low molecular weight oligomers.<sup>12,13</sup> The resulting polymer from ROMP contains carbon-carbon double bonds along the whole polymer chain. Since this cause decreasing the thermal stability, in industry use, it is often hydrogenated for final products. In addition polymerization of norbornene there is no need further modification.



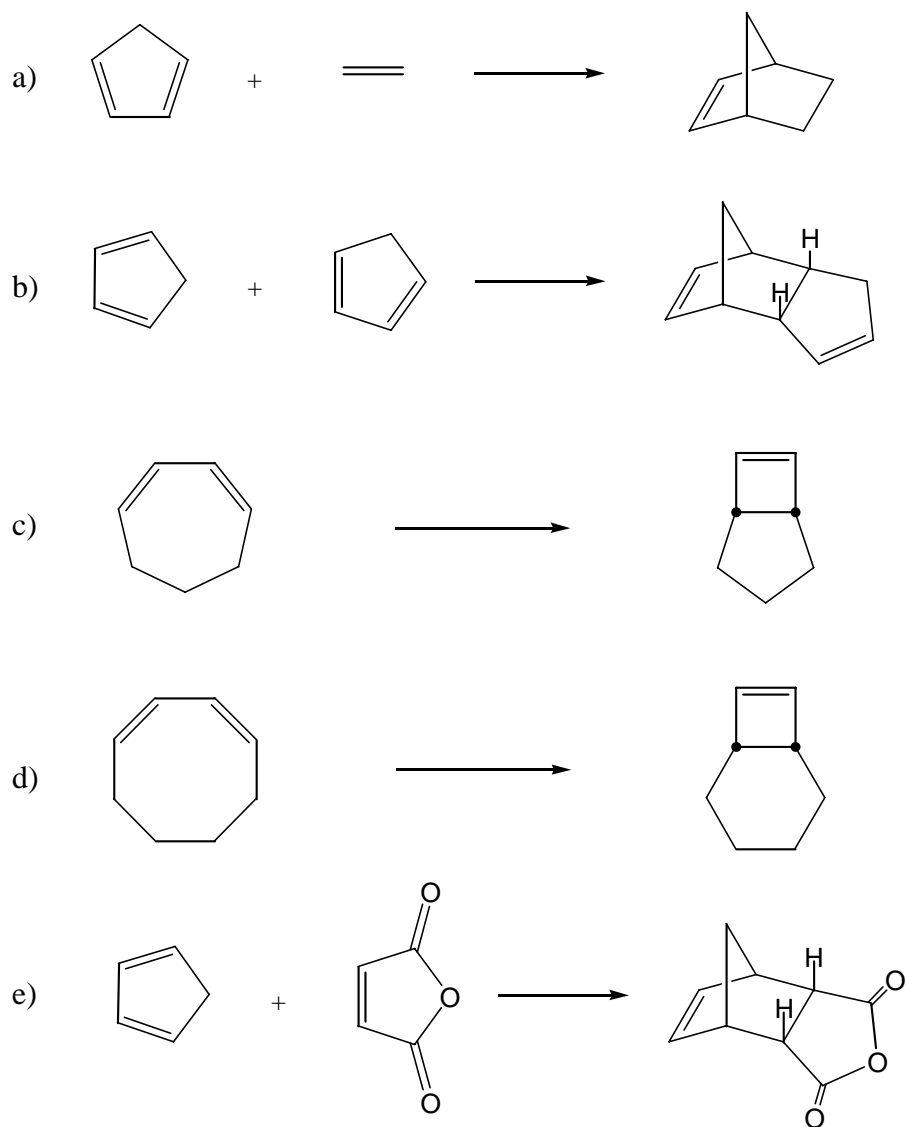
**Figure 1.3:** Mechanism of ROMP (norbornene is shown as monomer).

Diels-Alder reaction between ethylene and cyclopentadiene produces norbornene. By virtue of cleanness and simpleness of Diels-Alder reaction, norbornene is fairly cheap and readily available. Polynorbornene (ROMP or addition polymer) are not yet as popular as commodity materials like polyethylene or polypropylene, though their superb properties and the evolution of metal catalyst systems make polynorbornene excellent candidates for specialty materials. This implies that other similar fused ring or cyclic olefins also have a potential to make unprecedented materials.

### 1.3 Cyclic Olefins

During the past four decades, several examples of addition polymerization of monocyclic olefins such as cyclopropene,<sup>14</sup> cyclobutene<sup>15</sup> and cyclopenten<sup>16</sup> or fused ring olefins such as norbornene<sup>17-19</sup> using coordination-insertion catalyst systems have been reported. Even with ROMP, suitable polymerization technique, cyclic olefin is rarely utilized in polymer industries, except for norbornene, dicyclopentadiene and their derivatives.<sup>10</sup> Cyclic olefins are barely utilized and are not paid a great deals of attention despite their potential.

It is noteworthy that many types of cyclic olefins can be prepared through pericyclic reactions.<sup>20</sup> For instance, norbornene is prepared from ethylene and cyclopentadiene through Diels-Alder reaction<sup>21-23</sup> and cyclopentadiene dimer forms readily through a Diels-Alder reaction. Also 1,3-cyclic diene such as 1,3-cycloheptadiene or 1,3-cyclooctadiene frameworks yields bicyclic olefin through intramolecular 2+2 cycloaddition reaction. The significance of these types of reactions is that simple reactants give desired cyclic structure in high yield, reaction carries out in high regiospecific and stereospecific manner, and there is no need of other reagents and no by products. Furthermore, the pericyclic reactions are fairly tolerant with various functional groups. Hence, wide variety of cyclic olefin derivatives is available, Figure 1.4.



**Figure 1.4:** Pericyclic reactions a) Diels-Alder reaction between cyclopentadiene and ethylene b) Dimerization of cyclopentadiene c) 1,3-cycloheptadiene to bicyclo[3.2.0]-hept-6-ene d) 1,3-cyclooctadiene to bicyclo[4.2.0]oct-7-ene e) Diels-Alder reaction with functional group

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## Chapter 2: Ring Opening Metathesis Polymerization (ROMP) in Water

### 2.1 Introduction to ROMP

#### 2.1.1 Brief History of ROMP

In the Merriam-Webster dictionary,<sup>1</sup> it quotes the word “metathesis” as follows.

Function: Noun

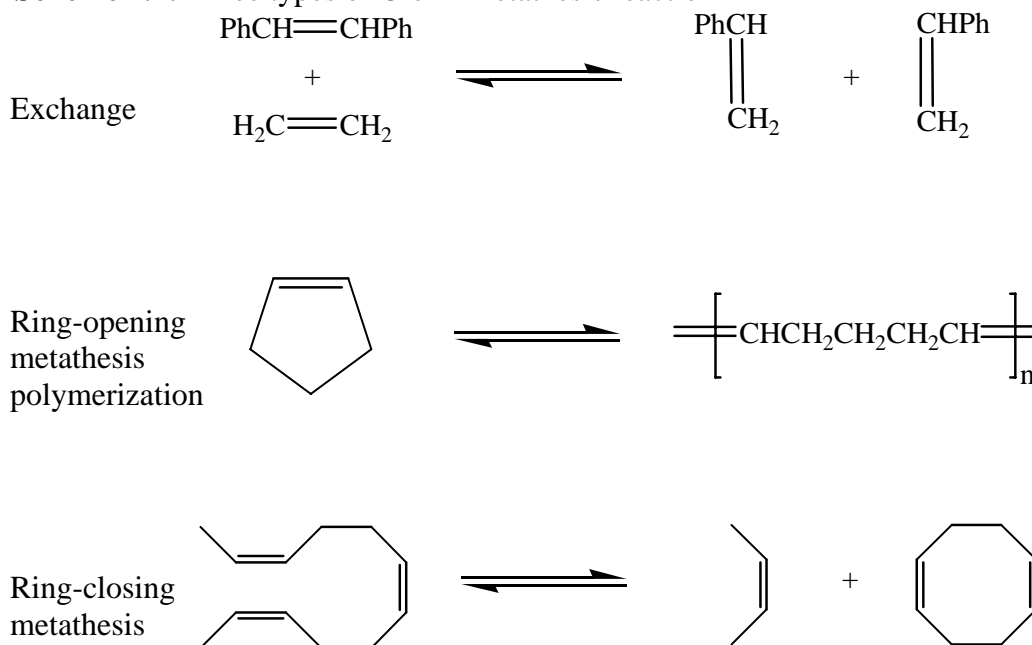
Etymology: Late Latin, from Greek, from *metatithenai* to transpose, from *meta-* + *tithenai* to place—a change of place or condition: as

a) transposition of two phonemes in a word

b) a chemical reaction in which different kinds of molecules exchange parts to form other kinds of molecules.

In olefin chemistry metathesis describes the apparent interchange of carbon atoms in a pair of carbon-carbon double bonds. Olefin metathesis reactions fall into three broad classes in which the overall chemistry is represented in Scheme 2.1.

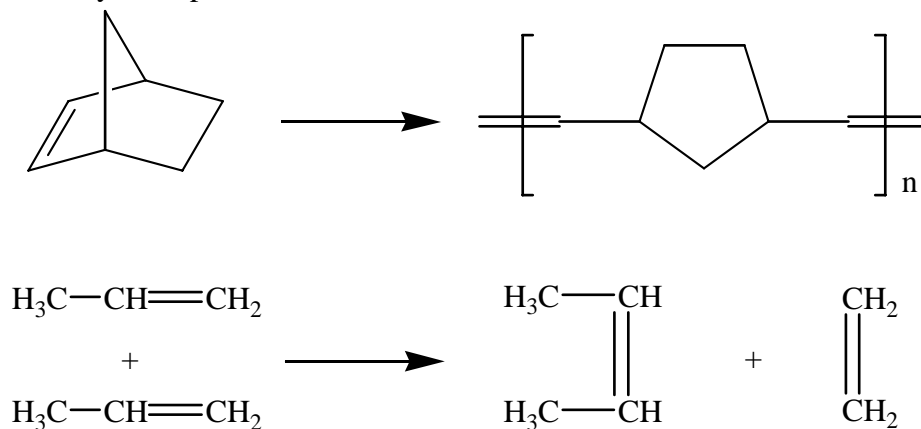
**Scheme 2.1:** Three types of Olefin metathesis reaction



The reactions are generally reversible and, with right catalyst system, equilibrium can be attained in a matter of seconds, even with substrate/catalyst ratios of  $10^4$ , it is indeed remarkable reaction.<sup>2</sup>

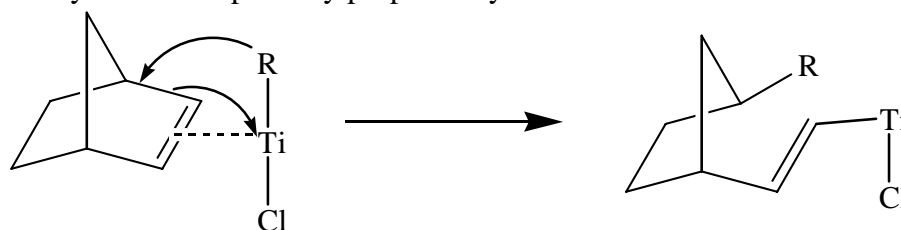
In 1960, first open publication of olefin metathesis reaction was during the investigation of Ziegler-Natta polymerization, led by Truett, of strained cyclic olefins, such as norbornene.<sup>3</sup> Structural studies on the polymer obtained from a Ziegler-Natta type  $\text{TiCl}_4/\text{Et}_3\text{Al}$  catalyzed polymerization of norbornene revealed an unexpected result.<sup>3</sup> Instead of obtaining the fully saturated polymer expected from a coordination-insertion mechanism, the product polymer still possessed carbon-carbon double bonds, indicating that the polymerization had occurred by some sort of ring-opening process, the mechanism of which was still undefined. In 1964 independent from this polymerization reaction, Banks reported olefin exchange reaction between two propylene molecules (disproportionation) catalyzed by  $\text{MoO}_3/\text{Al}_2\text{O}_3$ , Scheme 2.2.<sup>4</sup> Earlier than these reports, Eleuterio<sup>5</sup> and Peters<sup>6</sup> have filed patents for polymerization and disproportionation reactions, respectively.

**Scheme 2.2:** Early examples of olefin metathesis reactions



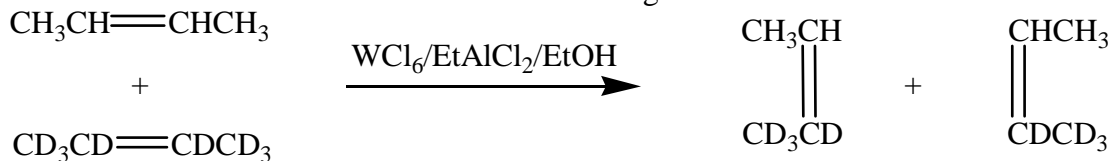
After realization of the reaction, the attention moved to its mechanism. Since two different catalyst systems were catalyzing each type of reaction, the connection between them was not immediately apparent. Truett proposed reaction pathway for norbornene polymerization in his first report, Scheme 2.3, but his proposal does not involve double bond cleavage.<sup>3</sup>

**Scheme 2.3:** Polymerization pathway proposed by Truett.



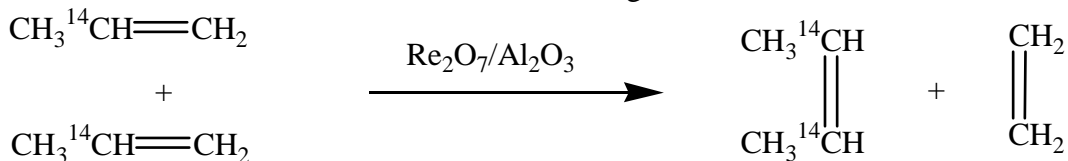
The discovery of  $\text{WCl}_6/\text{EtAlCl}_2/\text{EtOH}$  (1/4/1) catalyst system that catalyzed not only the polymerization of cycloocta-1,5-diene but also the disproportionation of pent-2-ene led to the realization that they were one and same chemical reaction.<sup>7-9</sup> Furthermore, the reaction between but-2-ene and but-2-ene- $\text{d}_8$  led only to but-2-ene- $\text{d}_4$ , Scheme 2.4, demonstrates the remarkable fact that the double bonds are completely broken in the reaction, leading to an exchange of alkyliden moieties.<sup>7,8</sup>

**Scheme 2.4:** The confirmation of double bond cleavage-recombination



Independently, Mol provided evidence for double bond cleavage by using [2-<sup>14</sup>C]propene reaction.<sup>10</sup> Radioactivity is not found in the ethene, Scheme 2.5.

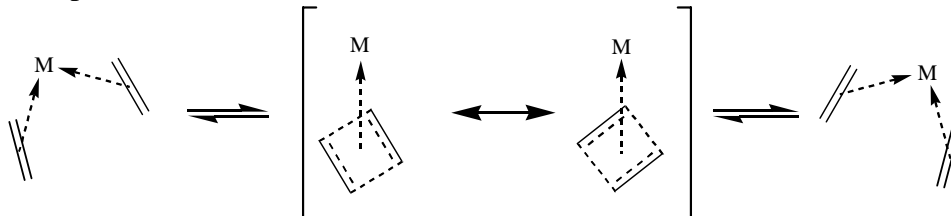
**Scheme 2.5:** Another evidence of double bond cleavage



A different approach was required to prove that the double bond is completely broken during ring opening polymerization of cycloalkenes. Dall'Asta prepared copolymers of [1-<sup>14</sup>C]cyclopentene/cyclopentene catalyzed by WOCl<sub>4</sub>/Et<sub>2</sub>AlCl/(PhCOO)<sub>2</sub> system. After complete degradation of the copolymer by ozonolysis and following conversion into the α, ω-diol acetates, all of the <sup>14</sup>C is essentially localized in AcO(CH<sub>2</sub>)<sub>5</sub>OAc. If the ring opening had happened at single bond, a different result would have been obtained.<sup>11</sup>

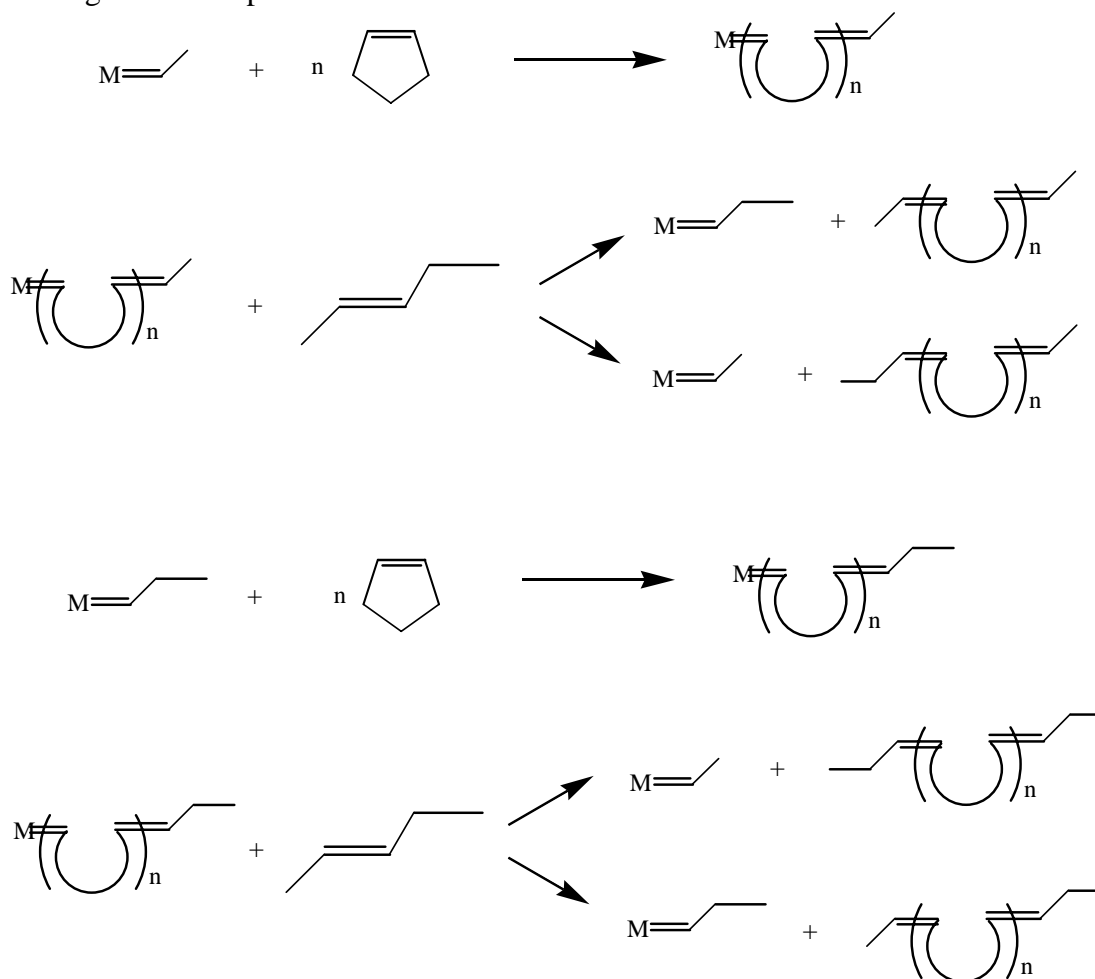
The first plausible proposed mechanism is the so-called “pair-wise” mechanism, Scheme 2.6. According to this proposal, the catalyst center brings two olefin moieties into the same vicinity, then exchange double bond so as to form new olefin molecules.<sup>12</sup>

**Scheme 2.6:** “pair-wise” mechanism

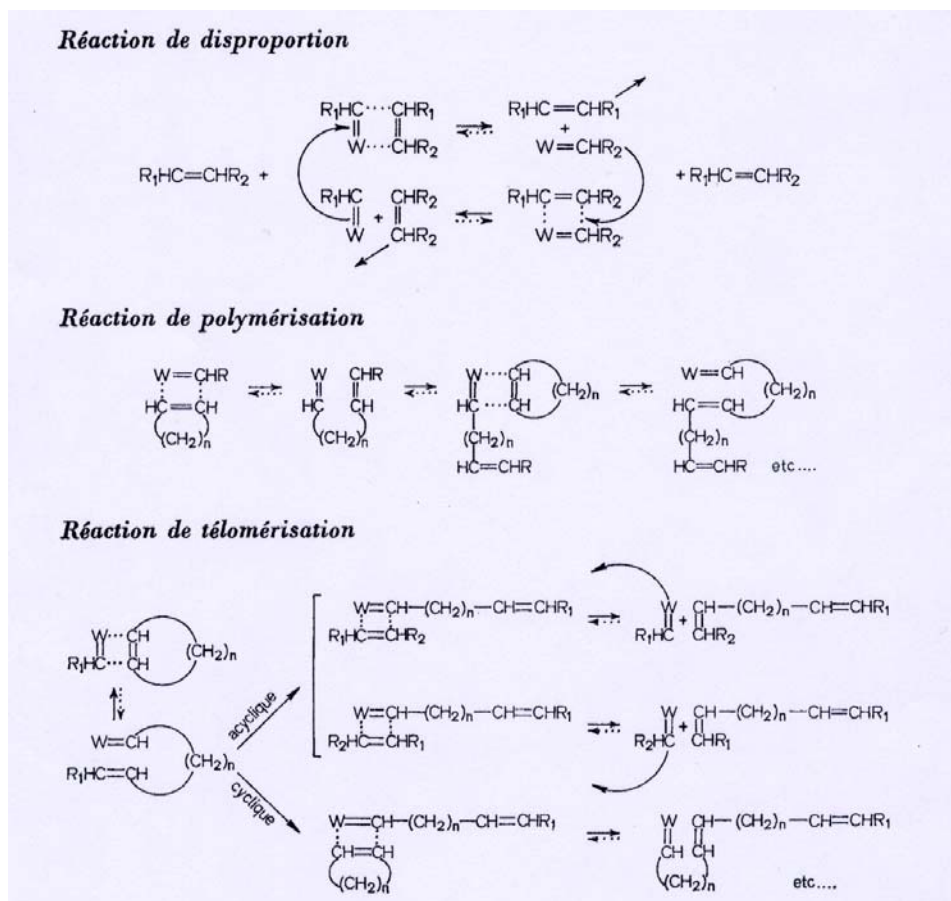


However the cross-metathesis reaction of cyclopentene with unsymmetrical olefin pet-2-ene catalyzed by  $\text{WOCl}_4/\text{Bu}_4\text{Sn}$  or  $\text{WOCl}_4/\text{Et}_2\text{AlCl}$ , Herisson observed that the products of reaction consisted of three series of compounds, Scheme 2.7, namely  $\text{E}(\text{CP})_n\text{E}$ ,  $\text{E}(\text{CP})_n\text{P}$  and  $\text{P}(\text{CP})_n\text{P}$ , where E represents ethylidene, P represents propylidene and  $(\text{CP})_n$  represents n units of open ring cyclopenten. These series were formed in the statistical ratio 1:2:1 even in the initial product. This observation led to the proposal of the metal carbene mechanism, since direct pair-wise exchange of double bonds would yield only the unsymmetrical series.

**Scheme 2.7:** An evidence for metal carbene mechanism. Cross-metathesis reaction, scrambling olefin components

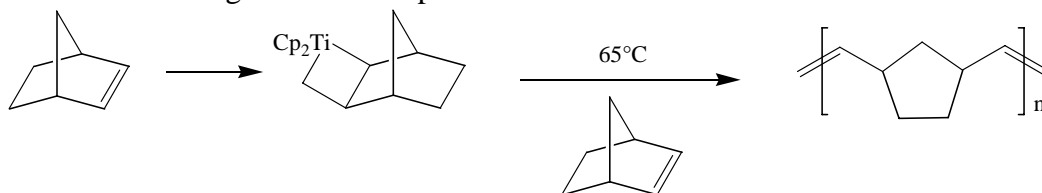


In 1970, Herrison and Chauvin proposed the metal carbene mechanism in their report,<sup>13</sup> Figure 2.1. Tebbe and his co-workers reported first clean and direct observation of metal carbene species with well-characterized titanium system in 1978.<sup>14,15</sup>

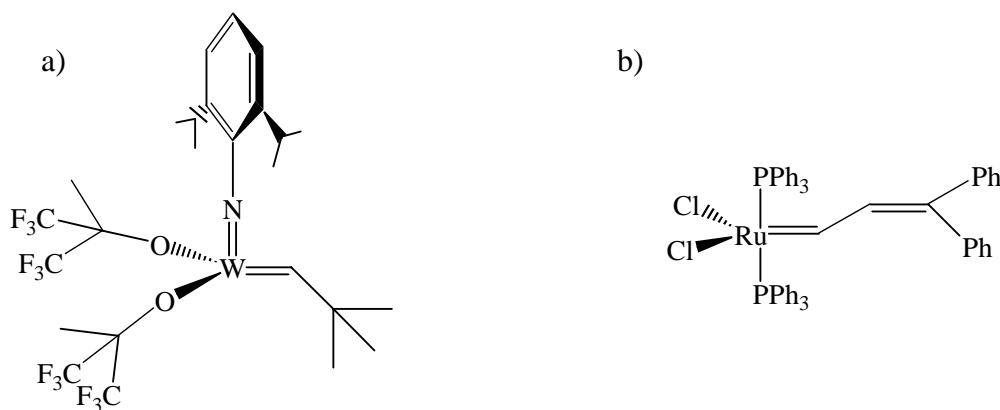


**Figure 2.1:** Proposed mechanism by Chauvin. (Reproduced from *Die Makromolekulare Chemie* **1970**, 141, 161)

**Scheme 2.8:** First living ROMP example.

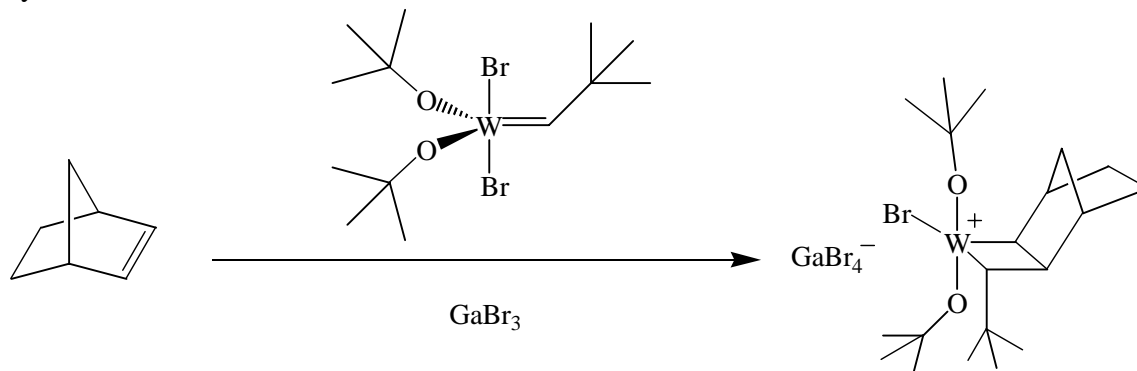


In 1984, Grubbs reported the first living polymerization system for the ring opening metathesis polymerization with titanacyclobutane / titanium carbene complex, Scheme 2.8.<sup>16,17</sup> In 1986, Schrock reported the first imido-alkoxy complex of the  $W(CHR')(N-2,6-C_6H_3-iPr_2)(OR)_2$  ( $R=OCMe(CF_3)$ ,  $R'=tBu$ ), Figure 2.2, which showed a higher activity than titanacyclobutane / titanium carbene complex in cross-metathesis reaction, however chain transfer reaction was observed in ROMP of norbornene at room temperature.<sup>18,19</sup> Improvement to reduce chain transfer for ROMP is achieved by changing the alkoxide group to  $OC(Me)_2CF_3$ . In 1987, Osborn and co-workers reported first direct observation of chain-propagating metal-carbene and metallacyclobutene species during ROMP of norbornene using tungsten base catalyst,<sup>20</sup> Scheme 2.9. In 1992, Grubbs and co-workers reported the synthesis of the first well-defined ruthenium carbene complex,<sup>21</sup> which catalyzed ROMP of norbornene, Figure 2.2.



**Figure 2.2:** Early example of well-defined catalysts a) Schrock type b) Grubbs type

**Scheme 2.9:** First direct detection of metallacyclobutene complex during norbornene polymerization.



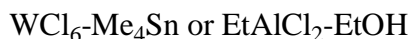
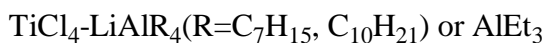
As we can see that through this history, although the olefin metathesis reaction was found in 1950s, its development and mechanistic studies flourished in 1980s. For their frontier work for developing and understanding the olefin metathesis reaction, Chauvin, Schrock, and Grubbs are recognized as Nobel Prize winner in 2005.

### 2.1.2 The Classification of ROMP Catalyst

The mechanism of olefin metathesis reaction has been shown to involve metal carbene complexes and metallacyclobutenes. However such intermediate has never been identified or isolated in most active catalytic systems.

According to recent understanding of metathesis catalysts, it is classified into three types; (I) those consisting of an alkyl or allyl group in one of the components, (II) those consisting of an actual metal carbene, and (III) those having neither a preformed carbene nor an alkyl group component

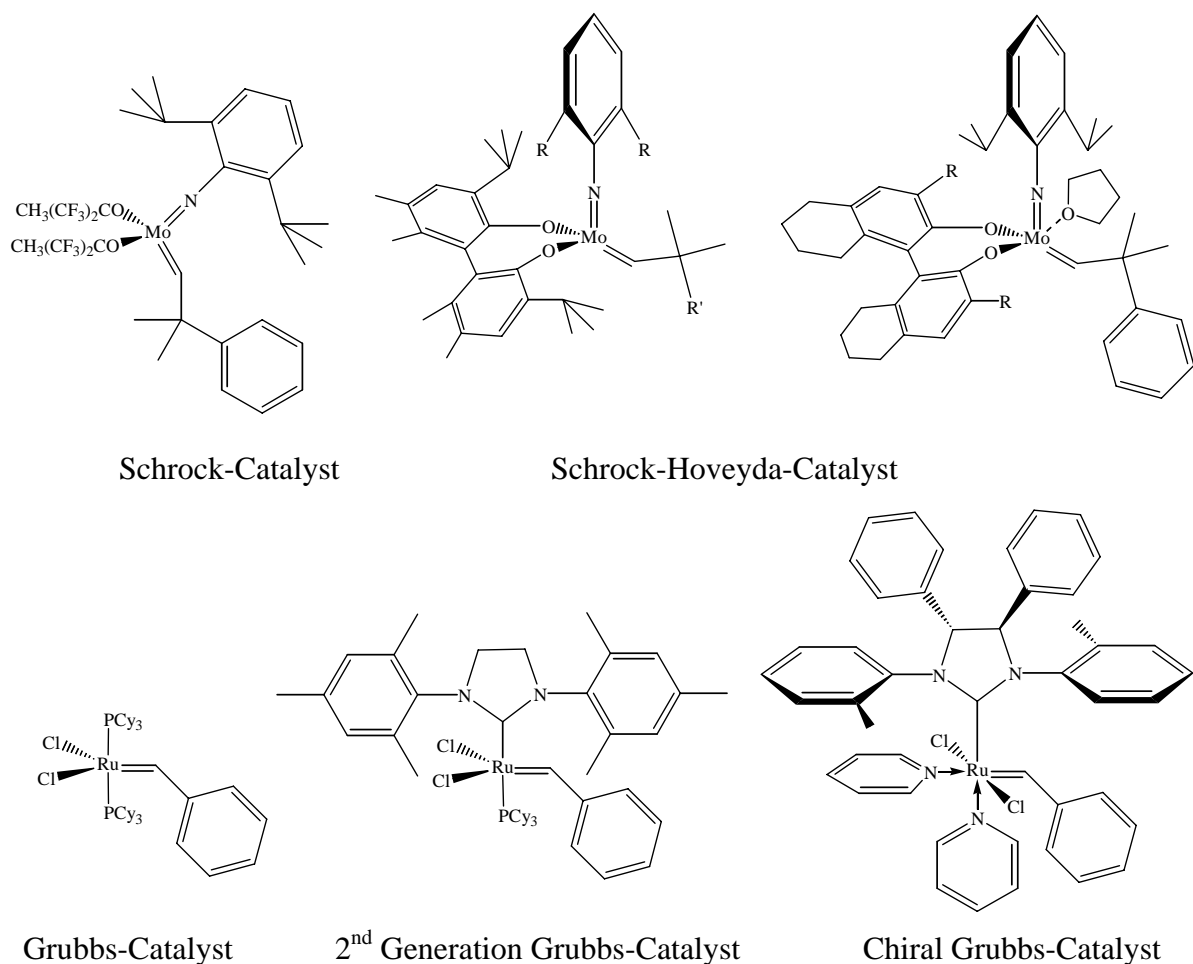
Type I catalyst systems consist of several components; a metal halide, a cocatalyst and sometimes a third component such as an alcohol, Figure 2.3.



**Figure 2.3:** Metal halide-metal alkyl olefin metathesis catalyst systems.

An alkyl agent cocatalyst may have several functions. Most likely, it may alkylate the transition metal center that then can be converted to a carbene complex by reductive elimination. It may also reduce transition metal to lower oxidation states and to open up sites for the coordination. It may also act as ligand to transition metal in some way.<sup>2</sup> Nonetheless, the reactive species is not well-defined and broad disperse polymer samples are usually obtained, this type of catalyst systems are often used in industrial application because of its availability of chemicals, the low processing cost and their good stability. One needs to be extremely careful to activate this catalyst system as activity depends on several factors, order of addition of reagents (olefin is not even last component), temperature and sometime these systems require “aging”.

Type II catalyst systems are the most advanced, most sophisticated and well-defined systems, Figure 2.4. They are all bearing a carbene moiety and carefully designed to be stable enough to handle. Employing well-characterized catalyst systems with known structure and activities ensure reaction outcome such as, stereochemistry.



**Figure 2.4:** Carbene Ligand Transition Metal Olefin Metathesis Catalyst

In the molybdenum system, Schrock and his co-workers did a lot of frontier investigations, and hence these catalysts are well known as the Schrock type catalyst.<sup>22,23</sup> The Schrock type catalysts are very active and somewhat tolerant with functional groups during ring open metathesis polymerization.<sup>24,25</sup> In 1993, first chiral molybdenum carbene catalyst was introduced.<sup>26</sup> Then, Schrock and Hoveyda developed more active chiral molybdenum carbene catalyst system, they are so-called the Schrock-Hoveyda catalysts.<sup>27-29</sup> Although

these molybdenum based catalysts systems are highly active, one needs to use extreme care of moisture and oxygen to handle.<sup>30</sup>

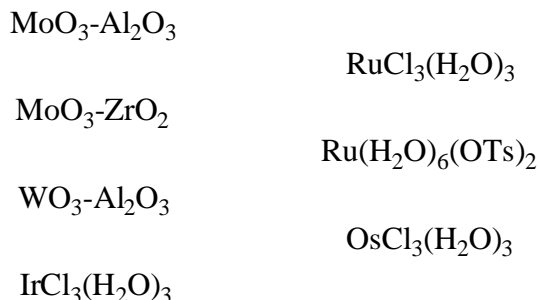
On the other hand, Grubbs and his co-workers did the intensive works on ruthenium catalyst systems, now those are called Grubbs catalysts, Figure 2.4.<sup>30-34</sup> An advantage of the ruthenium-based catalysts over the molybdenum-based catalysts is its stability. Because of the less oxophilic nature of ruthenium metal, Grubbs catalysts are stable in ambient atmosphere. In addition, Grubbs catalysts are highly active and show living polymerization character even in water medium.<sup>31,35</sup> Very recently, Grubbs and Hong reported the first highly active water soluble ruthenium carbene complex for olefin metathesis reactions.<sup>36,37</sup>

The examples of Type III catalysts are listed in Figure 2.5. In this type of catalyst systems, metal carbene is formed by interaction of the substrate olefin itself with transition metal center.

Molybdenum-based catalysts are generally more effective than corresponding tungsten based ones. Many kinds and combination of supports ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ) can be used. The catalytic activity is strongly influenced by type of support, surface metal content and calcination temperature. This type of heterogeneous catalyst system is easy to be used in large scale and in the gas phase reaction. Therefore, supported molybdenum oxide catalyst systems have received much attention and they are widely used in petrochemical process, such as SHOP process.<sup>2</sup>

On the other hand, late transition metal species, ruthenium, osmium and iridium, are often used as the hydrated form. Since the first discovery of olefin metathesis reactions with ruthenium complexes, trichlororuthenium hydrate, had been realized to catalyze ring opening

metathesis polymerization in refluxing ethanol and in water, however, the polymerization yields were low.<sup>38,39</sup>



**Figure 2.5:** Catalysts with no alkyl agent and preformed carbene

In the late 1980s, the potential of ruthenium catalysts for olefin metathesis reaction again resurfaced. Trichlororuthenium hydrate catalyzed ROMP, however, along with long induction period (typically ~24 hours) in organic solvent.<sup>40</sup> To reduce the induction time, more strictly anhydrous conditions were employed, but this caused induction time even longer. Quite unexpectedly, however, ring opening metathesis polymerization initiated after only 30 minutes in aqueous solution. Water was found not only to shorten the induction time but also to be compatible with this catalyst system. This is also because of aforementioned less oxophilicity of ruthenium metal. Novak reported that the ruthenium aqueous solution can be recycled at least 14 times without any loss of activity, and even with progressive smaller induction period.<sup>41</sup> These remarkable discoveries brought much attention to the simple ruthenium complex as olefin metathesis catalysts in green chemistry point of view.<sup>40-44</sup>

## 2.2 Target Polymerization

### 2.2.1 Green Chemistry

The evolution of technology has been improving our standard of living. However, since the Industrial Revolution the scale and severity of environmental pollution has also been getting worse. Technology used to be developed to improve the efficiency, the quality and the cost of products, but environmental concern were lacking. In the 1960s, environmental pollution got much popular attention, which is represented by the fact that the United States Congress passed the Clean Air Act in 1963 or the National Environmental Policy Act (NEPA) is was signed by U.S. President Richard Nixon in 1970.<sup>45</sup>

“Green Chemistry” or “Sustainable Chemistry” is an umbrella concept that is defined by the design, development, and implementation of chemical products and process to reduce or eliminate the use and generation of substances hazardous to human health and the environment.<sup>46</sup> Paul T. Anastas itemized this definition as follows.<sup>47,48</sup>

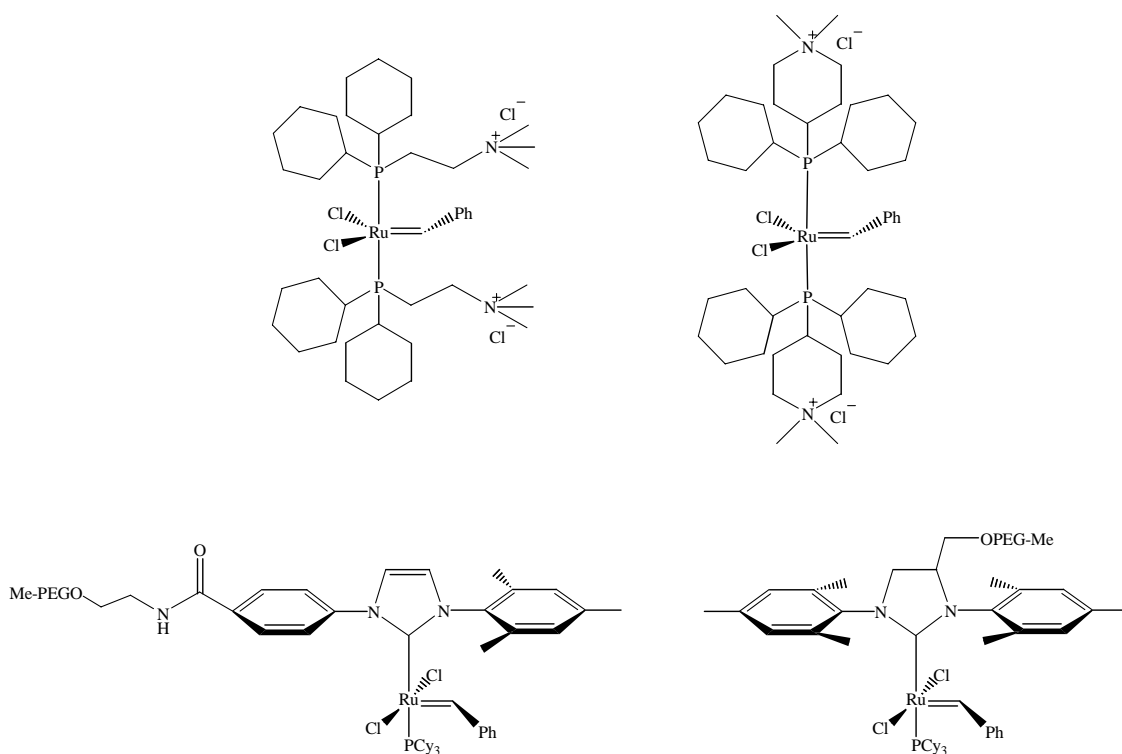
- Prevention of waste/by-product
- Maximum incorporation of the reactants (starting materials and reagents) into the final product.
- Prevention or minimization of hazardous products.
- Designing of safer chemicals.
- Energy requirement for any synthesis should be minimum.
- Selecting the most appropriate solvent.
- Selecting the appropriate starting materials.
- Use of the protecting group should be avoided.
- Use of catalysts should be preferred.
- Products obtained should be biodegradable.
- The manufacturing plants should be so designed as to eliminate the possibility of accidents during operations.
- Strengthening of analytical techniques to control hazardous compounds.

In other words, “Greener” reaction is that requires no solvent or non-hazardous solvent, and produces no by-products.

As mentioned earlier (*Section 2.1.2*), olefin metathesis ruthenium catalyst works well in water medium, and catalyst can be recycled.<sup>40-44</sup> Ring opening metathesis polymerization in water is ideal candidate for the Green Chemistry.

### 2.2.2 Olefin Metathesis Ruthenium Catalyst (Background)

Grubbs and his co-workers have been making a great effort to develop a family of ruthenium carbene complex for olefin metathesis reaction and ROMP in water/aqueous medium.<sup>49-51</sup> Very recently, Grubbs and his co-worker reported new highly active water-soluble ruthenium catalyst, Figure 2.6.<sup>36,37</sup>



**Figure 2.6:** Water-Soluble ruthenium carbene complex for olefin metathesis reactions.

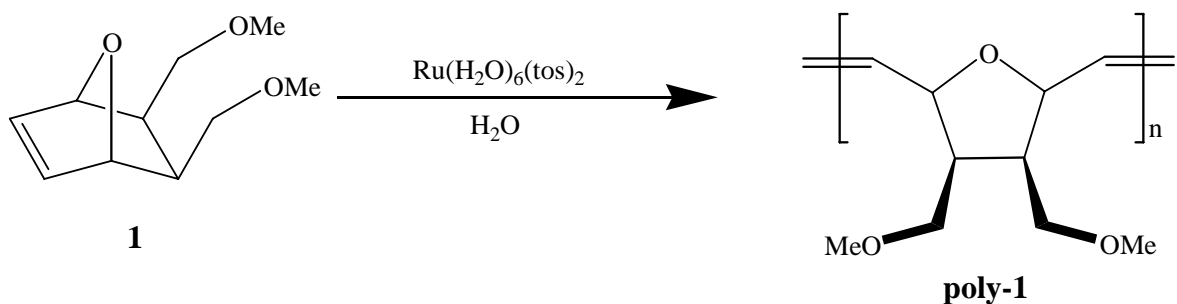
A water-soluble character of ruthenium complexes is achieved by introduction of tertiary amine or polyethylene glycol moieties to the Grubbs' catalysts. These preformed carbene complex shows precise control over the reaction. For instance in ROMP, molecular weight control and living nature of polymerization is observed.<sup>50</sup> Although the preformed water-soluble ruthenium carbene complex possesses distinguished properties, its preparation requires several steps from raw materials.

Precedence of the water-soluble ruthenium carbene complex, in 1960s simple ruthenium salts, like trichlororuthenium hydrate, had been found to catalyze ROMP of strained cyclic olefins in alcoholic or aqueous solvents emulsified system, at elevated temperature.<sup>38,52-54</sup> However low molecular weight and low yield were obtained.

Late 1980s, Novak and Grubbs extensively explored potential of simple ruthenium salts as ROMP catalyst in aqueous medium. Trichlororuthenium hydrate was found to catalyze the ROMP of functionalized monomers, such as 7-oxanorbornene and its derivatives in organic solvent. Long induction period typically ~24 hours was observed without adding water. In fact, water acts as co-catalyst in this catalytic system. The ROMP polymerization can be carried out in water alone as a solvent, addition to this fact, catalyst can be recycled up to 14 times without any detectable loss of activity. In these aqueous ROMP systems, initiation rate is increased by 5,000-fold compare to solely organic solvent system.  $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$  (tos = p-toluenesulfonate) was also found a highly active ROMP catalyst in water, Scheme 2.10.<sup>40,41,55</sup> These extraordinary tolerance toward functional group and water had never been obtained other than ruthenium metal. This character summarized in Table 2.1.<sup>31</sup>

Molecular model studies indicate these poly(7-oxanorbornene) backbone has ability to form helical structures with all of the tetrahydrofuran oxygens facing into the interior of the helix, Figure 2.7.<sup>40</sup> This unique helical conformation could act as acyclic ionophores when it is in solution.<sup>56</sup> These remarkable capabilities of ruthenium open the door to new class of chemistries and materials.

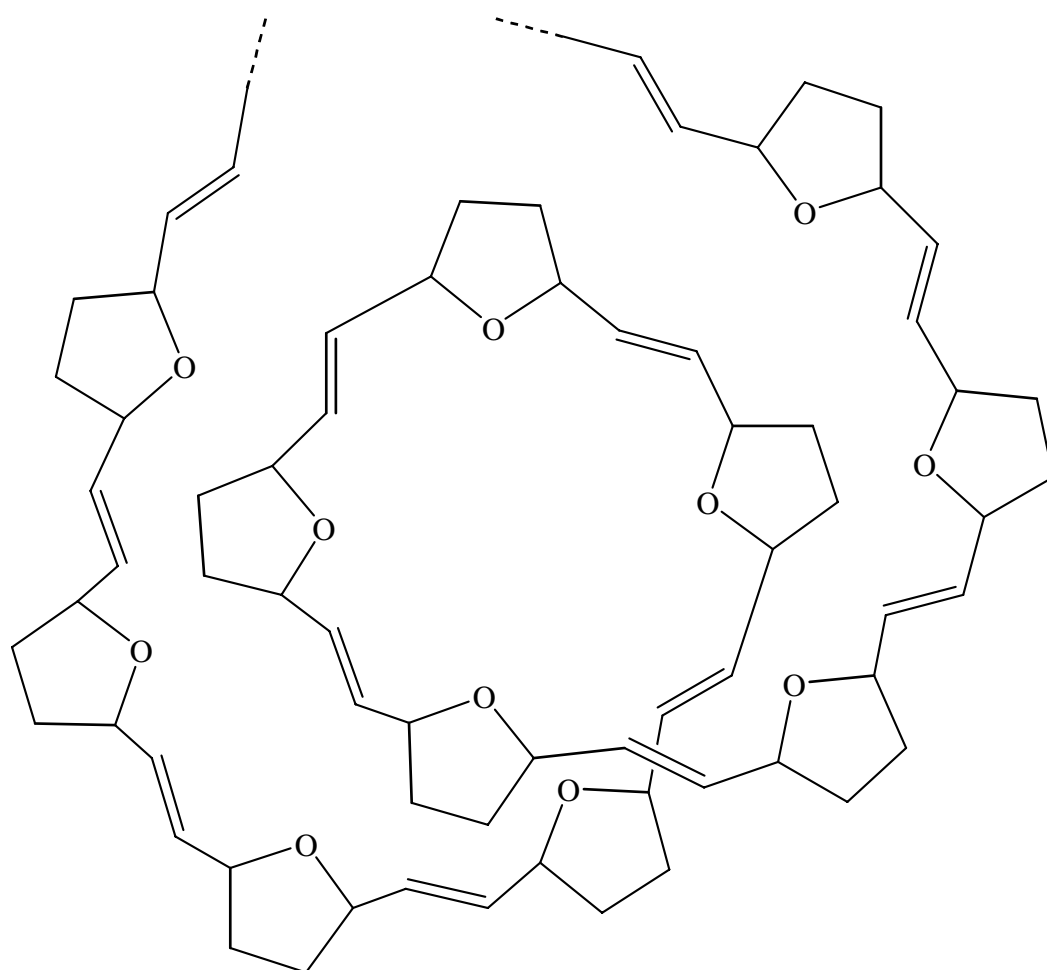
**Scheme 2.10:** ROMP of 7-oxonorbornene derivatives in water catalyzed by simple ruthenium salt.



**Table 2.1:** Functional group tolerance of transition metal olefin metathesis catalysts

	<b>Titanium</b>	<b>Tungsten</b>	<b>Molybdenum</b>	<b>Ruthenium</b>
	Acids	Acids	Acids	<i>Olefins</i>
	Alcohols, water	Alcohols, Water	Alcohols, Water	Acids
	Aldehydes	Aldehydes	Aldehydes	Alcohols, Water
	Ketones	Ketones	<i>Olefins</i>	Aldehydes
	Esters, Amides	<i>Olefins</i>	Ketones	Ketones
	<i>Olefins</i>	Esters, Amides	Esters, Amides	Esters, Amides

Reactivity ↑

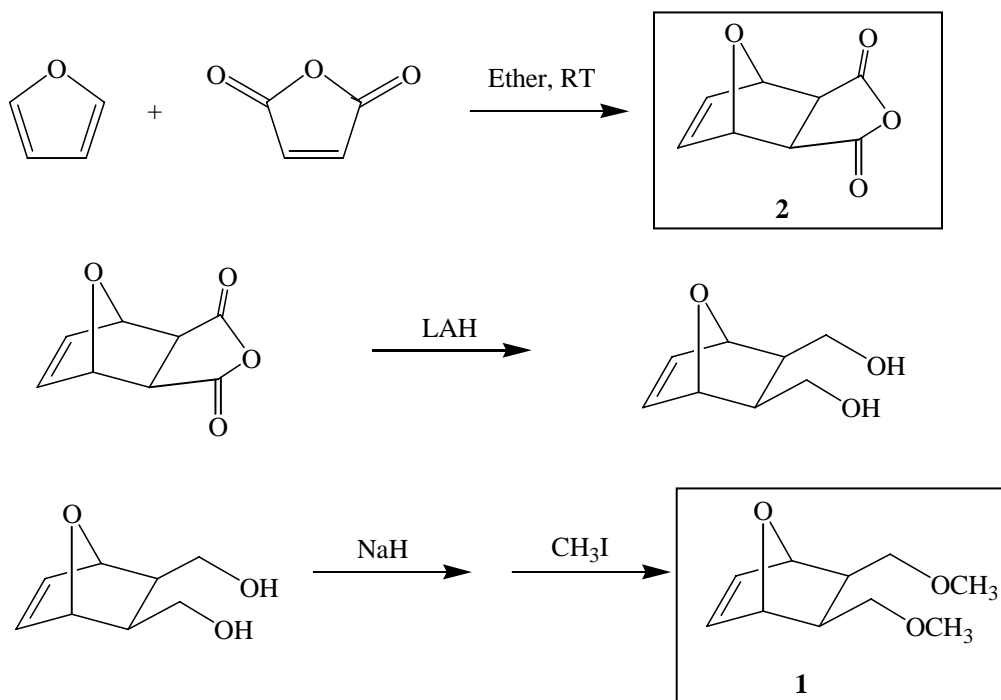


**Figure 2.7:** Ion binding cavity formed from a helical turn of poly(7-oxonorbornene)

### 2.2.3 New Monomer

Finding of an important role of water in ROMP with simple ruthenium complex encouraged further investigation of ROMP in aqueous media. Monomer **1**, 5,6-bis(methoxymethyl)-exo-7-oxabicyclo[2.2.1]hept-2-ene, was successfully polymerized using  $\text{RuCl}_3(\text{H}_2\text{O})$  or higher active  $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$ . Preparation of **1** requires multiple steps from readily available starting materials, furan and maleic anhydride, Scheme 2.11. Although reactions involved this route are simple and straight forward, it still contains multiple steps. If compound **2**, exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, is utilized as a monomer for ROMP in water, it will be a good example of the potential of ROMP from the “green chemistry” and material science point of view.

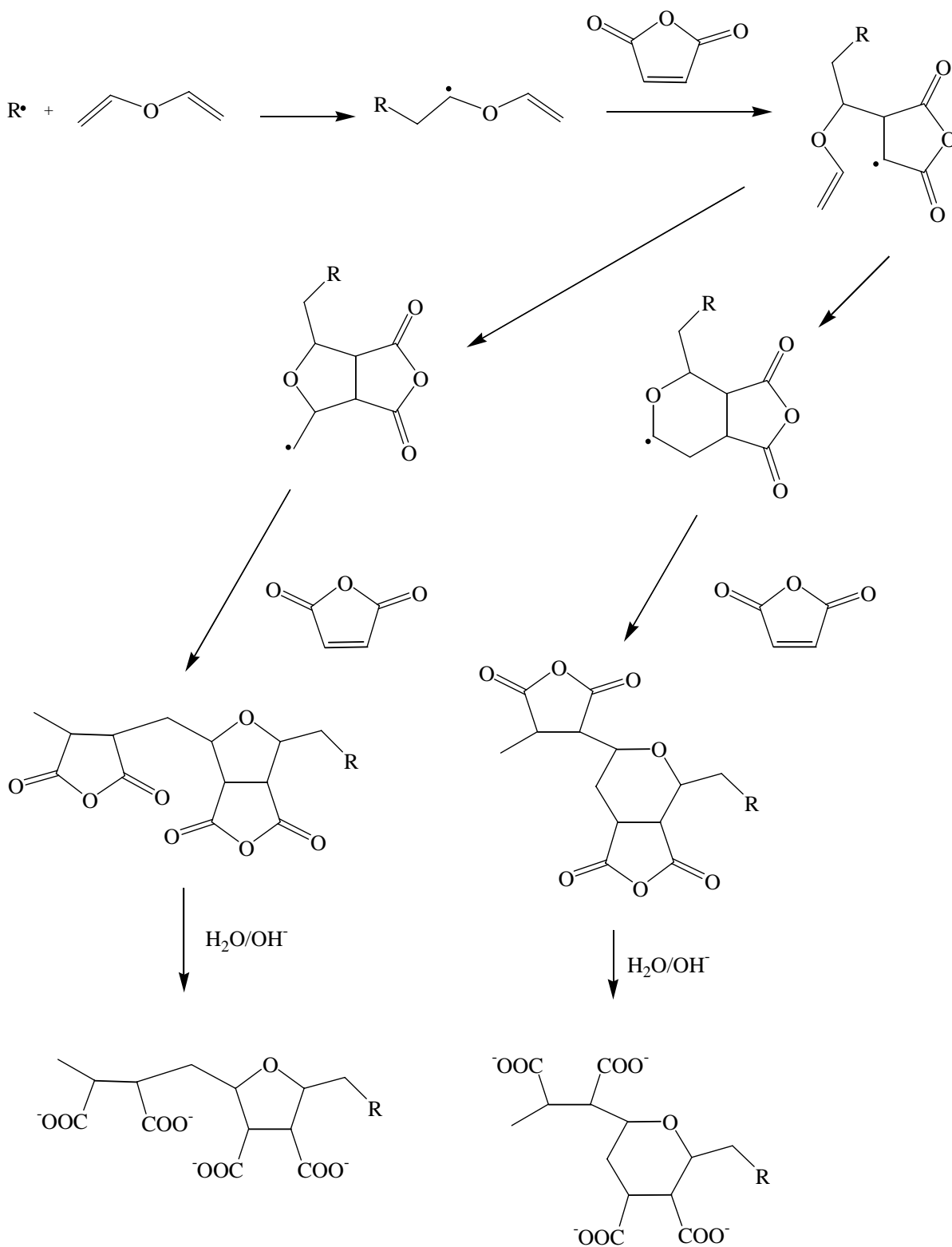
**Scheme 2.11:** Synthetic route to monomer **1** from furan and maleic anhydride



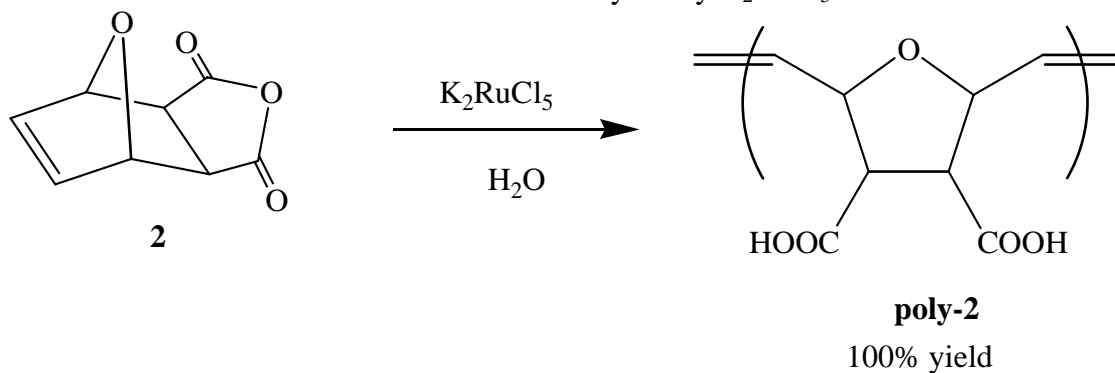
Water-soluble, polyanionic materials are important class of synthetic polymers. One example of those materials is hydrolyzed copolymer of maleic anhydride and divinyl ether by free-radical polymerization, Scheme 2.12. This type of polyanionic material has been extensively investigated because it possess of important properties such as, poly-electrolyte, antitumor activity, antiviral activity, drug delivery system, and polymer adsorbants.<sup>57-65</sup> Despite these impressive properties, advancement of these polyanionic materials has been limited. This is due, in part, to lack of control over polymerizations and the lack of new monomers. This lack of control is actually a fatal issue in the maleic anhydride-divinyl ether system, because high molecular weight materials are toxic. Thus, not only high molecular weight materials are to be avoided, but also broad molecular weight distributions are equally undesirable. The free radical polymerization provides little control over regioselectivity of cyclization steps and stereoselectivity of propagation steps. These little control characters through polymerization complicate the composition and the character of materials.

Several years ago, in our group, the polymerization of compound **2** in water is achieved using simple ruthenium salt,  $K_2RuCl_5$ , after more than 30 kinds of ruthenium complexes were investigated.<sup>55</sup> Monomer **2** is obtained by one step Diels-Alder reaction of furan and maleic anhydride and resulting polymer possess polyanionic form because the anhydride group is hydrolyzed during polymerization, Scheme 2.13. . This polymerization demonstrates a great potential of ROMP from the aforementioned points, “greener” polymerization and provides a well controlled polyanionic architecture.

**Scheme 2.12:** Copolymerization of maleic anhydride / divinyl ether



**Scheme 2.13:** ROMP of monomer **2** in water catalyzed by  $K_2RuCl_5$



#### 2.2.4 Problem and Objective

Unfortunately, the polymerization of monomer **2** was not reproducible. Monomer purity,  $H_2O$  purity, temperature, concentration, and solution pH were examined to find out what caused unexpected ill-reproducibility. None of those variables influenced the result: Finally, we turned our attention to the source of  $K_2RuCl_5$  and we examined ruthenium complexes, and discovered several discrepancies between vendors.

In this study, we focus on catalyst. We obtained four different samples of  $K_2RuCl_5$  from different sources and examined all four systematically to uncover the problems with polymerization and identify true catalyst precursor.

### 2.3 Preparation of monomer

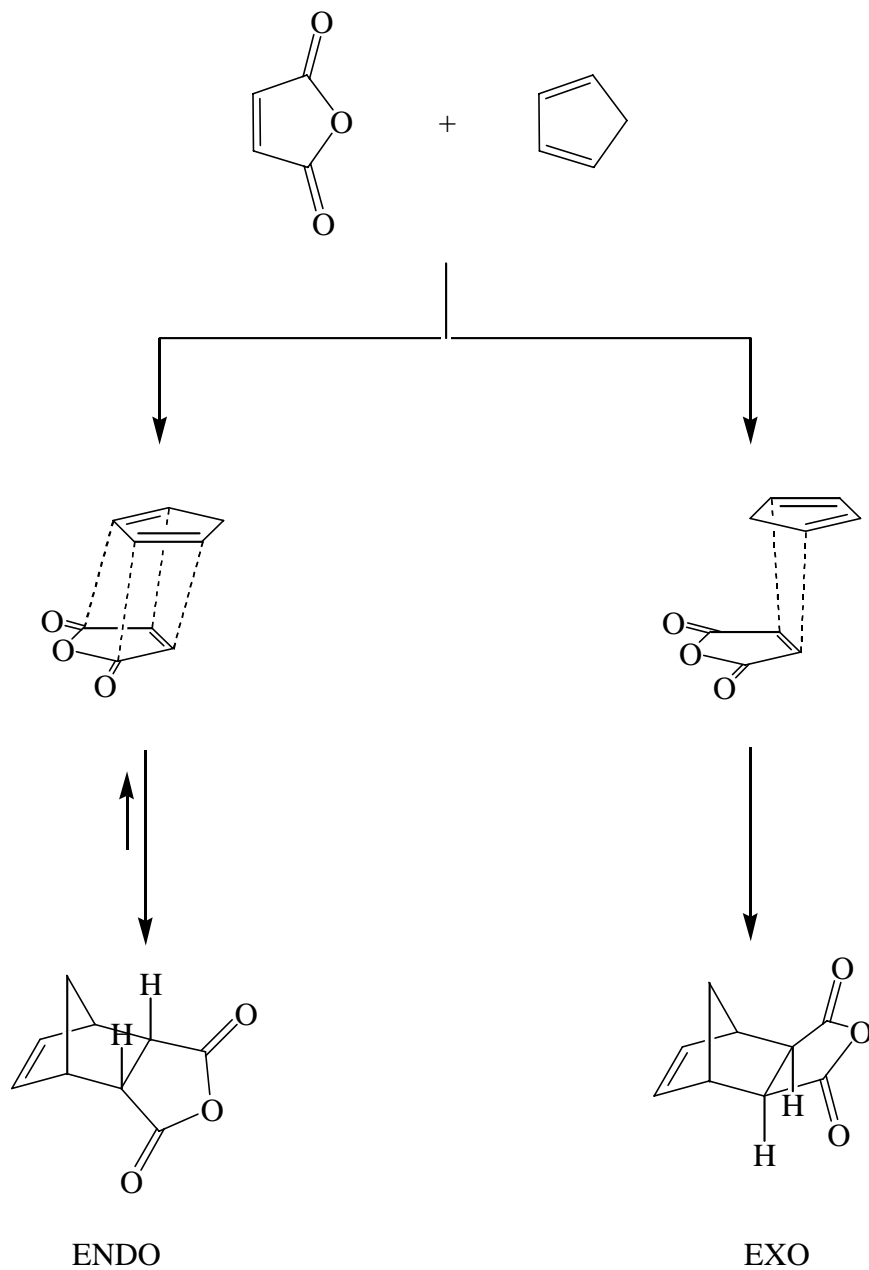
#### 2.3.1 Diels-Alder reaction

$[4\pi+2\pi]$  cycloaddition reactions are known as the Diels-Alder reaction. Diels-Alder reaction is one of best-known reactions, which is widely used to construct six membered rings with well control the regio- and stereo-chemistry over the four possible stereoisomers.

The *exo* addition is expected to be preferred because it suffers fewer steric repulsive interactions than the *endo* approach, however most of the cases, reaction proceeds *endo* selective. This *endo* selectivity is explained by *stabilizing secondary orbital interactions*, Scheme 2.14. The *endo* preference is known as Alder's rule.<sup>66</sup>

A typical example is the reaction of maleic anhydride with cyclopentadiene that, at room temperature, gives the *endo* adduct. However, at 200°C, the *endo* adduct is converted to the thermodynamically more stable *exo* adduct through a retro-Diels-Alder reaction followed by re-addition, Scheme 2.14.

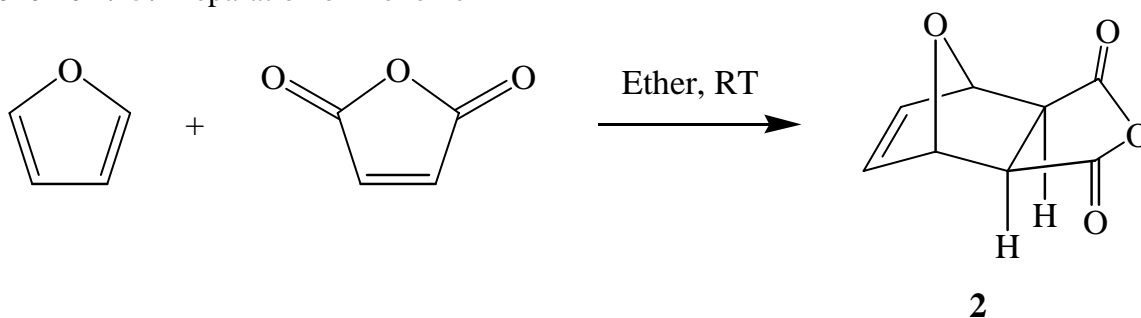
**Scheme 2.14:** Diels-Alder reaction; endo, exo selectivity in the case of maleic anhydride and cyclopentadiene.



### 2.3.2 Stereo Selectivity

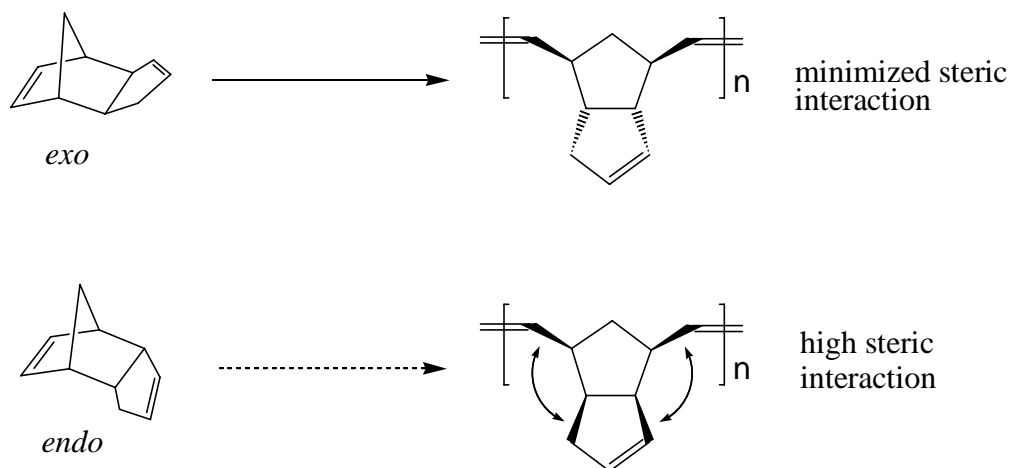
Preparation of monomer **2** is depicted in Scheme 2.15. Monomer **2** is synthesized successfully through a Diels-Alder reaction of maleic anhydride with furan in diethyl ether at room temperature. Monomer **2** is directly obtained as pure crystal from reaction mixture with high yield up close to 90%, and no further purification is required. Interestingly, monomer **2** is formed solely *exo* adducts even at room temperature.

**Scheme 2.15:** Preparation of monomer **2**



This unusual *exo* preference is examined by two groups in a way of experiments and simulations.<sup>67,68</sup> There is little discrepancy between two reports though, substantially they reached same conclusion. Kinetically favored *endo* adduct forms a little faster than thermodynamically favored *exo* adduct, same as in other Diels-Alder reactions, in the initial stage. However, Gibbs free energy difference of two transition states, *endo*- and *exo*-structure, is little as 0.25~0.56 kcal/mol, depends on calculations.<sup>67</sup> Steady reversible reaction can be attained even at room temperature. Hence, after certain period of reaction time, Diels-Alder reaction between maleic anhydride and furan yields only the thermodynamically favored *exo* adduct. We also suspect that the first formed *endo* adduct is soluble in ether, whereas the *exo* is not, thus precipitating out during the reactions.

Unexpected high *exo* selectivity of monomer **2** is beneficial to us in two ways. First, monomer is always provided in 100% purity without any tedious purification steps. This is very important especially in industrial application and in “green chemistry” aspect. Secondary, this is essential to this reaction; *endo* monomers polymerize reluctantly by ROMP fashion. In contrast to *endo* structure, *exo* monomer readily polymerizes by ROMP. Different reactivity between two isomers upon ROMP is explained by comparing the steric repulsion contained in the resulting two polymers, Figure 2.8. The polymer structure from *endo* isomer contains considerable steric repulsion in each repeating unit. On the other hand, the polymer structure from *exo* isomer doesn't contain such repulsion.



**Figure 2.8:** Steric repulsion in polymers obtained from *endo* and *exo* isomers of dicyclopentadiene.

## 2.4 Polymerization Study

### 2.4.1 Comparison of Commercially Available $K_2RuCl_5 \cdot H_2O$

In the previous study of the polymerization of **2** in aqueous medium, it is found that  $K_2RuCl_5$  can catalyze ROMP polymerization in water. The reaction is well-defined, however, it depends on the source of the Ru complex. We started this investigation by purchasing samples of four different brands of chlororuthenium potassium salts, Table 2.2. Actually, commercially available  $K_2RuCl_5$  is in a hydrate form. First, the appearances of salts were checked, Table 2.2. Two brands, Acros and Strem, complex have similar color (brown), and Aldrich has much brighter color (red-brown) and Alfa-Aesar has much darker color (black-brown).

**Table 2.2:** Ruthenium complex; Color of four different brands

Brand		Color
Aldrich	Potassium aquopentachlororuthenate (III) $K_2[RuCl_5(H_2O)]$	Red- Brown
Acros	Potassium pentachlorotuthenate (III) $K_2RuCl_5(H_2O)$	Brown
Strem	Potassium pentachlorotuthenate (III) hydrate $K_2RuCl_5 \cdot xH_2O$	Brown
Alfa Aesar	Potassium aquopentachlororuthenate (III) $K_2RuCl_5(H_2O)$	Black-Brown

### 2.4.2 Polymerization Activity

Next, these four different brands of ruthenium complexes were examined in the polymerization of monomer **2** in water, and the results are summarized in Table 2.3. Only Aldrich brand complex worked for the polymerization. Now, we know Aldrich is the one that we need, and other three brands could be some other similar formula ruthenium complex.

**Table 2.3:** Polymerization result

Run	Polymerization	Catalyst used	Color of Mixture
1	No	Strem	black
2	No	Strem	Initially dark orange, then red, then green
3	No	Strem	Initially dark orange, then red
4	No	Strem*	Dark red
5	No	Strem*	Dark red
<b>6</b>	<b>Yes</b>	<b>Aldrich*</b>	<b>Orange</b>
7	No	Alfa Aesar*	Black with red tint
8	No	Acros*	Dark reddish brown
<b>9</b>	<b>Yes</b>	<b>Aldrich</b>	<b>Light orange</b>

Reaction condition: monomer **2** 2.00 g, catalysts 0.025 g, H<sub>2</sub>O 7.0 ml, ~65C<sup>o</sup>, for 40 min

\*0.05 g of catalyst was used

We subjected Aldrich and Strem samples to elemental analysis, Table 2.4. The results clearly show that those two complexes contain different elements. The Aldrich one has some carbon in it, on the other hand, the Strem sample doesn't have hydrogen that means this complex is not a hydrate. At this point, we didn't know what the real catalyst precursor was. Basically those two complexes are close in composition. The real catalyst precursor could involve the tiny amount of carbon or similar formula complex, or different structure of isomers.

**Table 2.4:** Elemental analysis of two “K<sub>2</sub>RuCl<sub>5</sub>” samples.

	Aldrich		Strem
Element	Theory	Found	Found
H	0.5393%	0.49 %	0.0%
O	4.272 %	3.73 %	2.57 %
Cl	47.32%	47.24 %	47.49 %
C	0%	0.22%	0.0%

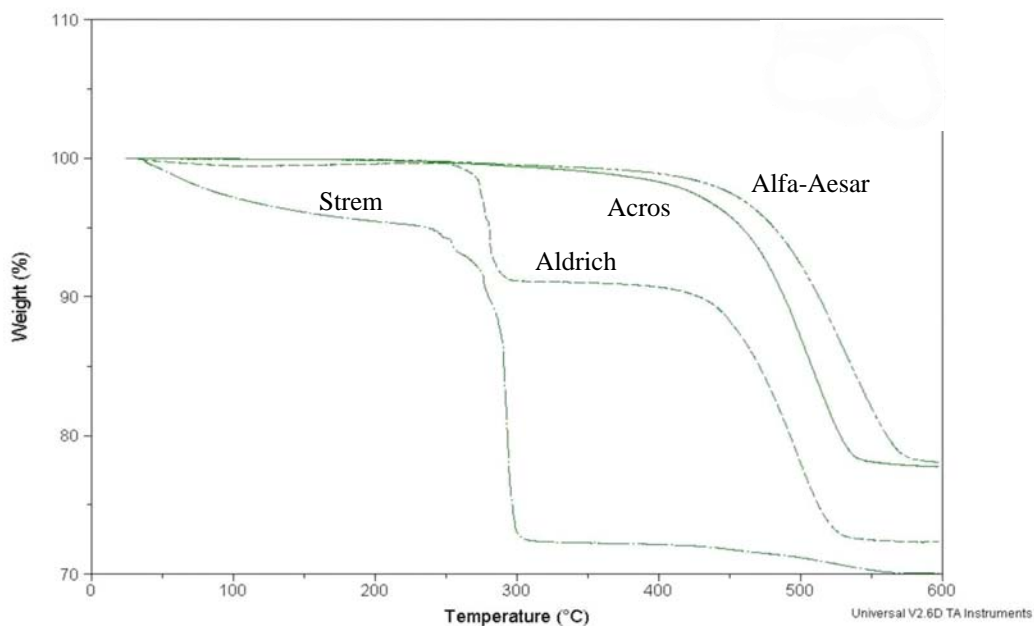
Just after the beginning of the 20<sup>th</sup> century, a series of papers on ruthenium chloride complexes can be found.<sup>69-75</sup> There was little controversy about real configuration of K<sub>2</sub>RuCl<sub>5</sub>·H<sub>2</sub>O, however, two different substances with, very similar or same formula, “K<sub>2</sub>RuCl<sub>5</sub>·H<sub>2</sub>O”, are reported. According to Howe two distinguishable complexes can be prepared from different routes and they show the same formula based on elemental analysis.<sup>70-75</sup> Howe names two different ruthenium complex for clarity of arguing as follows, rose prism crystalline ruthenium complex; potassium aquochlororuthenate K<sub>2</sub>Ru(OH<sub>2</sub>)Cl<sub>5</sub>,

and dark brown powder ruthenium complex; potassium ruthenium Trichloride  $K_2RuCl_5 \cdot H_2O$ .<sup>70,71</sup> Judging by the colors, aquochlororuthenate seems to be the Aldrich sample and ruthenium trichloride may be the three other brands. So, there might be a mistake with the labeling of the bottles. However, the carbon in the Aldrich sample has not been ruled out yet.

## 2.5 Revealment of the Real Catalyst precursor

### 2.5.1 Thermal Analysis of $K_2RuCl_5 \cdot H_2O$

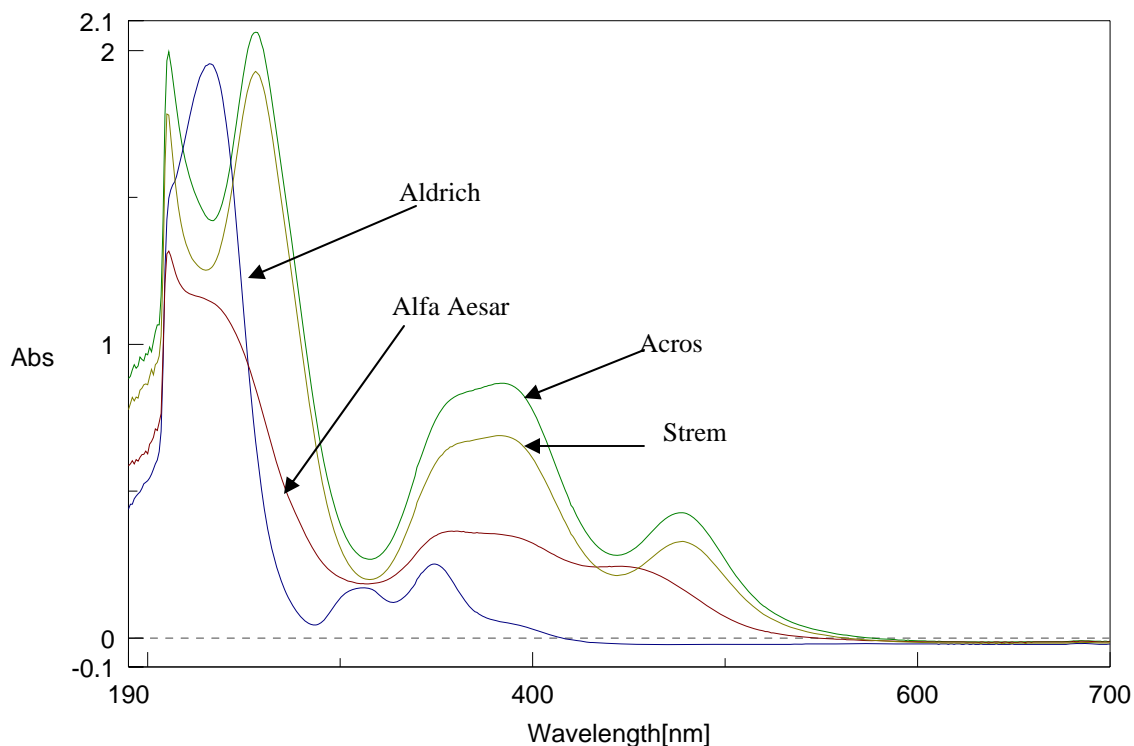
We examined thermal stability of those four samples by means of thermogravimetric analysis under a nitrogen atmosphere, Figure 2.9. Thermogravimetric analysis curves clearly show that there are three different samples; Acros and Strem seem to be identical. This result doesn't make sense based on Howe's argument, however we don't know the purity of samples and they could be mixtures of two different ruthenium complexes.



**Figure 2.9:** Thermogravimetric analysis of the four “ $K_2RuCl_5$ ” samples.

### 2.5.2 UV-Vis Analysis and pH Analysis of solution

To further elucidate these differences, we conducted UV analysis<sup>76</sup> and pH test<sup>77</sup> of these sample solutions, Figure 2.10 and Table 2.5.



**Figure 2.10:** UV analysis ( $10^{-6}$  M in 10 mL of 12 M HCl).

Both the UV and pH analysis support the proposal that the Acros and Strem samples are identical. The sample from Alfa Aesar seems to have characteristics of both the Aldrich and the Acros/Strem samples. In the UV spectrum, Alfa Aesar shows two absorbances around 380 nm and 430 nm, which show up on the Acros/Strem sample but not the Aldrich sample. From the pH analysis, again Alfa Aesar has pH values that lie between the other two sets of values. However, from these experiments, clear evidence was not provided.

**Table 2.5:** pH of aqueous solutions of the four samples of “ $\text{K}_2\text{RuCl}_5 \cdot n\text{H}_2\text{O}$ ”.

	Aldrich	Acros	Strem	Alfa Aesar
pH of water	5.84	5.72	6.05	6.02
Initial pH	4.71	4.47	4.50	4.57
after 3 minutes	3.95	3.48	3.53	3.60
after 5 minutes	3.71	3.26	3.34	3.35
after 7 minutes	3.61	3.16	3.20	3.30
after 9 minutes	3.56	3.09	3.10	3.23

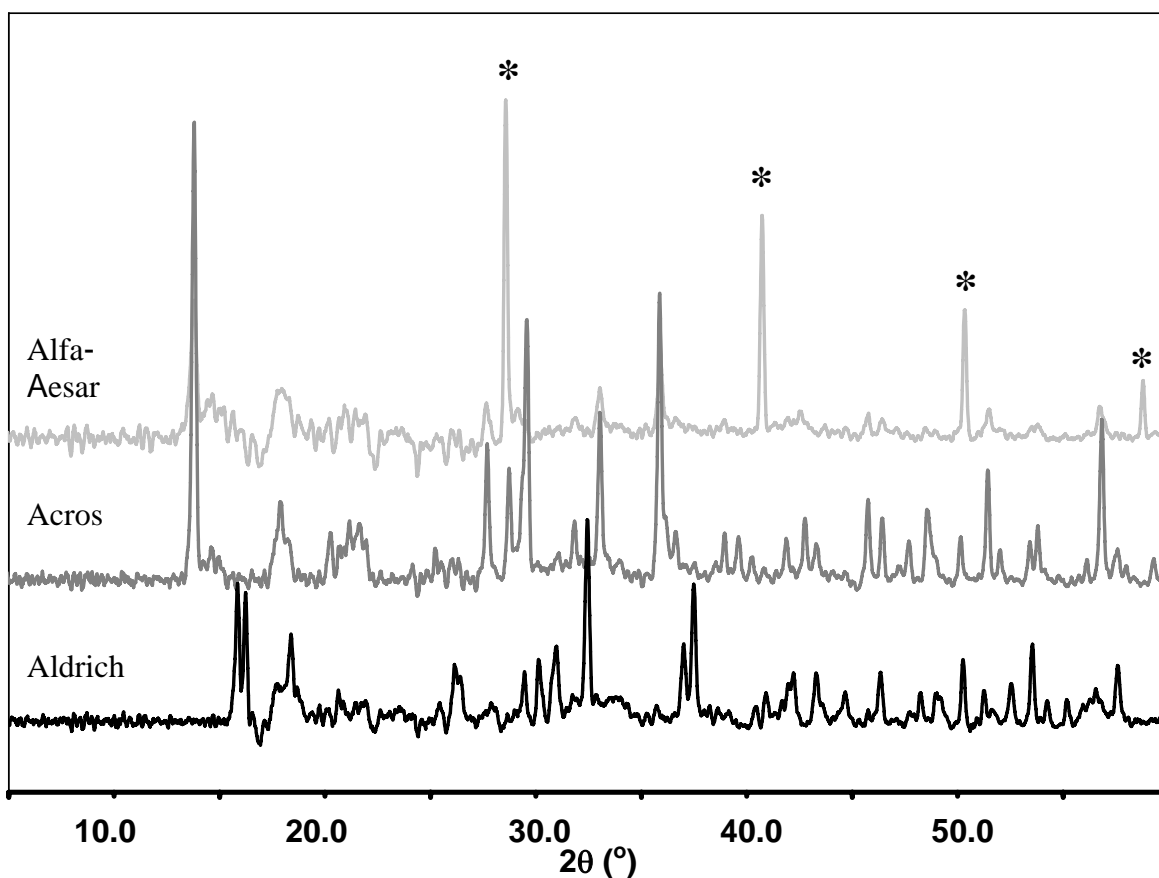
\*0.0936 g of each ruthenium salt was dissolved in 25 mL of water to test the pH. The pH was first taken of the water, then initially with the salt (before it had dissolved) and at 3, 5, 7, and 9 minute intervals for each of the four ruthenium salt brands.

### 2.5.3 X-ray Powder Diffraction

Unfortunately, it proved impossible to grow single crystal X-ray analysis quality crystals, so we subjected three of the samples, Aldrich, Alfa-Aesar and Acros, to powder diffraction studies. The three patterns were different, Figure 2.11. The Aldrich sample showed a pattern that matched the simulated pattern of  $\text{K}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$ . On the other hand, the Acros sample corresponded to the literature structure of  $\text{K}_4[\text{Ru}_2\text{Cl}_{10}\text{O}]$  which contains a  $\mu$ -oxo bridge between the two ruthenium(IV) centers.<sup>78,79</sup> The Acros sample is not

ruthenium(III). An X-ray powder diffraction pattern from Alfa-Aesar sample indicates mixture of  $\text{K}_4[\text{Ru}_2\text{Cl}_{10}\text{O}]$  and  $\text{KCl}$ . (Peaks with asterisks in Figure 2.11 corresponds to diffraction from  $\text{KCl}$ .)

The conclusion from X-ray powder diffraction is in good accordance with data from elemental analysis. Strem sample and Acros sample are confirmed identical species by TGA, UV and pH analysis. If Strem and Acros are  $\text{K}_4[\text{Ru}_2\text{Cl}_{10}\text{O}]$ , the theoretical chloride content is 48.6% and oxygen content is 2.2%. Experimental value from elemental analysis of Strem sample is that chloride content is 47.5% and oxygen content is 2.6%, Table 2.4.



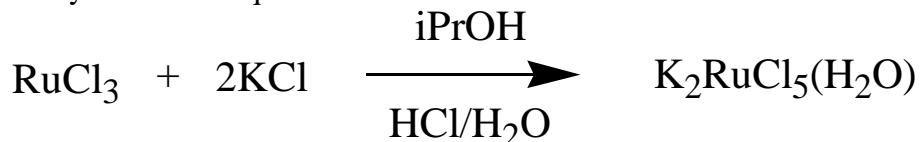
**Figure 2.11:** X-ray powder diffraction pattern of three “ $\text{K}_2\text{RuCl}_5$ ” samples

#### 2.5.4 Synthesis of $K_2RuCl_5 \cdot H_2O$

Taken in total, the Aldrich sample appears to be the “aquochlororuthenate” referred to by Howe.<sup>71,72</sup> And the active catalyst precursor for the ROMP of **2** in water is  $K_2RuCl_5 \cdot H_2O$ . However, the elemental analysis of the Aldrich sample shows contamination of a carbon residue. There might be small chance that this carbon residue has important role in the polymerization activity.

To eliminate the role of carbon present in the Aldrich sample, we synthesized our own “aquochlororuthenate” sample from ruthenium trichloride and potassium chloride, Scheme 2.16.<sup>69</sup> We obtained little darker color crystal compare to Aldrich sample salt. We polymerized **2** in water with the complex that we synthesized and it worked well. We now feel confident that  $K_2RuCl_5 \cdot H_2O$  is the real catalyst precursor and that the carbon impurity detected in the elemental analysis of the Aldrich sample does not play a role.

**Scheme 2.16:** Synthesis of “aquochlororuthenate”



## 2.6 Conclusion

The ring opening metathesis polymerization of monomer **2**, *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, in water has been reported.

Reproducibility problem with this reaction is examined by employing four different brands of potassium chlororuthenate hydrate salt,  $K_2RuCl_5 \cdot H_2O$ , obtained from Aldrich, Acros, Stem, and Alfa-Aesar.

Polymerization studies revealed that the Aldrich sample has activity toward ROMP of monomer **2** in water, whereas others do not. The following analyses of sample salts, thermogravimetric analysis, UV spectroscopy of solutions, and pH analysis of solutions provide the evidences of that Acros and Strem sample salts are identical.

X-ray powder diffraction analyses of three sample salts were performed. Diffraction pattern from Aldrich sample is in good agreement with simulated pattern of  $\text{K}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$ . In contrast, diffraction pattern from Acros sample shows characteristic peaks of  $\text{K}_4[\text{Ru}_2\text{Cl}_{10}\text{O}]$ , in which ruthenium has oxidation state four, ruthenium(IV). Alfa-Aesar sample is not pure form, it is mixture of  $\text{K}_4[\text{Ru}_2\text{Cl}_{10}\text{O}]$  and KCl.

We have also synthesized  $\text{K}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$  from ruthenium trichloride and potassium chloride. Synthesized  $\text{K}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$  has similar appearance of Aldrich sample and has same activity toward ROMP of monomer **2** in water as Aldrich sample salt.

The results from this study reveals that the active ruthenium catalyst precursor complex in the polymerization of **2** in aqueous medium is  $\text{K}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$ . This ruthenium complex can be prepared from simple ruthenium trichloride, and is also commercially available from Aldrich. Samples of “ $\text{K}_2\text{RuCl}_5\cdot\text{H}_2\text{O}$ ” purchased from Acros and Strem, are actually  $\text{K}_4[\text{Ru}_2\text{Cl}_{10}\text{O}]$  and are not active toward polymerization.

## 2.7 Experimental Section

### 2.7.1 General Procedures and Characterization

Maleic anhydride, furan and isopropanol were purchased from Aldrich Chemical Inc. and used as received. Ruthenium trichloride and potassium chloride were purchased from Strem Chemicals Inc. and used as received. Concentrated hydrochloric acid aqueous solution was purchased from Fisher Scientific. Water was purified through a reverse osmosis filter.

$^1\text{H}$ -NMR spectra were obtained using a Varian Mercury 400 (400MHz) spectrometers as specified. Chemical shifts are reported in  $\delta$  (ppm) and are referenced to selected residual proton peaks for the solvents as follows: 7.26 ppm for  $\text{CDCl}_3$  and 3.31 ppm for  $\text{CD}_3\text{OD}$ . Significant  $^1\text{H}$  NMR data are tabulated in the following order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br: broad), coupling constant in Hertz, number of protons.  $^{13}\text{C}\{^1\text{H}\}$  proton decoupled NMR were measured at 100 MHz on a Varian Mercury 400. Chemical shifts are reported in  $\delta$  (ppm) and are referenced to peaks of solvents as follows: 77.23 ppm for  $\text{CDCl}_3$  and 49.00 ppm for  $\text{CD}_3\text{OD}$ .

UV-Vis spectra were obtained using a Jasco V-550 spectrometer as solution in quartz cell. UV-Vis data are reported in wavelength (nm).

Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia.

### 2.7.2 Procedures

**Exo-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, 2.** Maleic anhydride (79 g, 0.80 mol) was dissolved in 600 mL of warm diethyl ether. Furan (55 g, 0.80

mol) was, then, added to this solution. After stirring this solution 3 days, a solid precipitate was formed. This precipitate was washed with 300 mL of cold diethyl ether. Precipitation was then dried under vacuum to yield 69 g of **1** (52% yield).  $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ )  $\delta$  6.59 (t,  $J = 1.0$ , 2H), 5.47 (t,  $J = 1.0$ , 2H), 3.19 (s, 2H)

**General procedure for polymerization of 2 by using ruthenium complexes.** Water (7 mL) was degassed by passing nitrogen through it for 10 min and then it was warmed up to 60 °C. Ruthenium complex (0.025g) was dissolved in this water followed by addition of monomer **2** (2.0 g 12 mmol). After 40 min of stirring, 1 M HCl solution to precipitate polymer. To purify the polymer, NaOH solution was added to polymer suspension to dissolve polymer, then acidified by HCl solution. The polymer was filtered, washed with water, and then dried under vacuum to yield 2.0 g of **poly-2**. (100% yield)  $^1\text{H-NMR}$  (400MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  5.72 (*trans*-olefin), 5.46 (*cis*-olefin), 5.02 (allylic), 2.90 (methane);  $^{13}\text{C}\{^1\text{H}\}$ -NMR (100MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  174.23 (carboxylate), 133.09 (olefin), 82.08 (*trans*-allylic), 78.96 (*cis*-allylic), 54.78 (methane).

**“Aquachlororuthenate”,  $\text{K}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$ .** Ruthenium trichloride (0.28g, 0.90 mmol) and potassium chloride (0.20g, 2.7 mmol) were dissolved in mixture of 45 mL of water and 45 mL of isopropanol. Concentrated HCl solution of 0.7 mL was then added. Resulting solution was refluxed for 20 min. Insoluble blackish powder filtered off. Solution was then put on bench top with cotton plug to recrystallize. Black/purple crystal of 0.23g was obtained. (67% yield)

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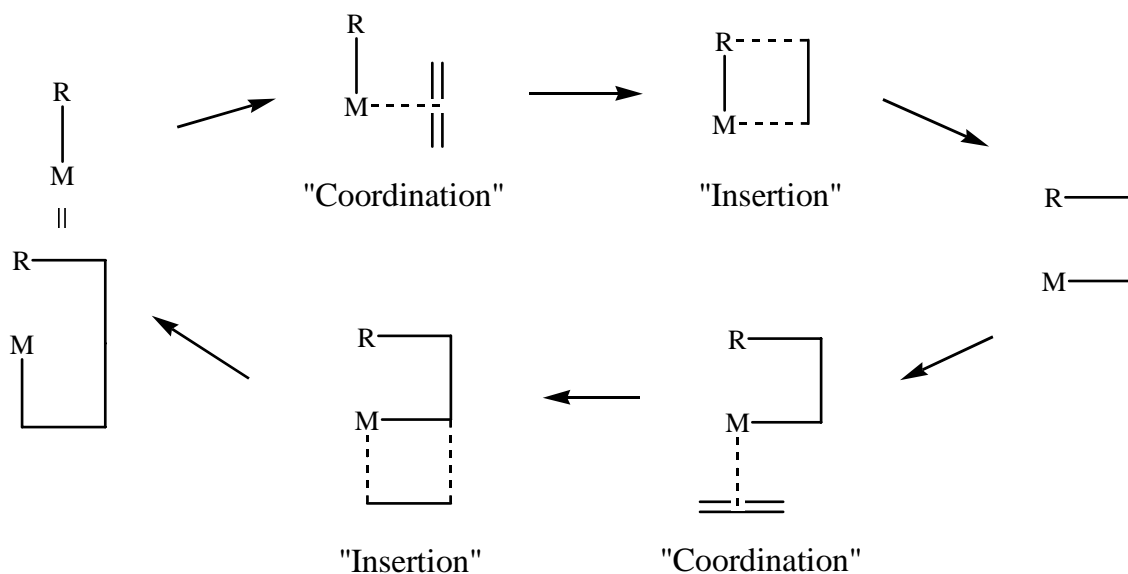
## Chapter 3: Polymerization of Cyclobutene Derivatives

### 3.1 Introduction of Coordination-Insertion Polymerization Catalyst

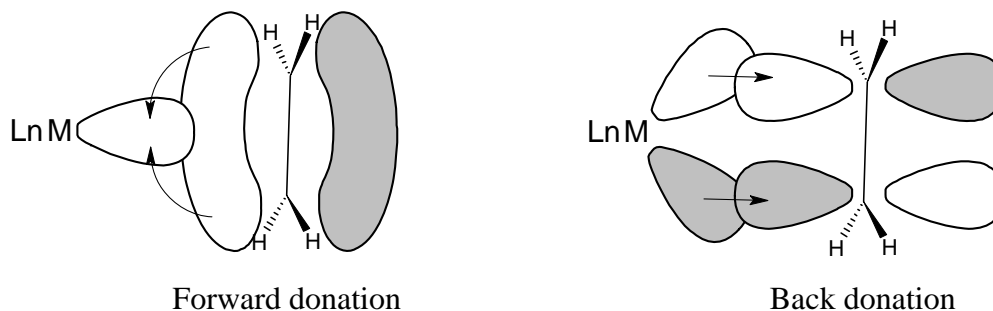
The mechanistic expression “Coordination Polymerization” was first proposed in the 1950’s, for the low-pressure polymerization of ethylene and propylene with the transition metal catalysts discovered by Ziegler and Natta.<sup>1,2</sup>

Nowadays, a polymerization in which polymer enchainment steps consist of monomer coordination to metal catalysts active site followed by monomer insertion to form covalent bond between metal center and ligand (alkyl) is referred to as “Coordination Polymerization” or in more detail a “Coordination-Insertion Polymerization”, Scheme 3.1. The basic mechanism of “Coordination-Insertion olefin polymerization” catalyzed by transition metal catalyst was proposed in 1960s by Cossee.<sup>3-5</sup>

**Scheme 3.1:** Mechanism of “Coordination-Insertion Polymerization”.



Olefin monomer coordination to the transition metal catalyst active center can be explained by overlapping olefin  $\pi$ -orbital and metal d-orbital. Figure 3.1 shows Dewar-Chatt-Duncanson model, the overlap of molecular orbitals involved in the formation of a metal-olefin bonding.<sup>1,6</sup>



**Figure 3.1:** Schematic presentation of olefin coordination to transition metal (Dewar-Chatt-Duncanson model)

The olefin  $\pi$ -bonding filled orbital donates its electrons to the transition metal through overlap with the metal d-orbital, forward donation, which results in an enhancement of the electron density at the metal center. When the transition metal has an occupied d-orbital, overlapping antibonding  $\pi^*$ -orbital with this filled d-orbital results in decreasing electron density at metal center and increasing electron density in the olefin  $\pi^*$ -orbital. This interaction is called back donation. Either one of above interactions stabilizes  $\pi$ -complexes and lowers the level of original orbital energy, which facilitates the insertion chemistry.

In the beginning of 1980s, so called the Kaminsky-Sinn homogeneous transition metal catalyst systems were found.<sup>7</sup> The Kaminsky-Sinn catalysts consist of titanium or zirconium metallocene complexes and large excesses of methylaluminoxane (MAO) as an activator/co-catalyst. The Kaminsky-Sinn catalysts are still considered as a sub-class of the

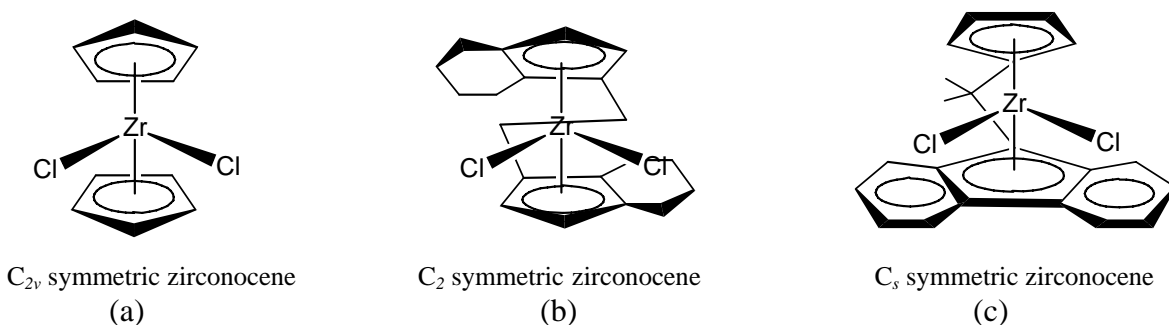
Ziegler-Natta catalysts. The major difference between conventional Ziegler-Natta catalysts and Kaminsky-Sinn catalysts is that Kaminsky-Sinn catalysts are homogeneous, well-defined single active site catalyst systems, whereas the conventional Ziegler-Natta catalysts are heterogeneous and ill-defined multi active site system. The significance of the discovery by Kaminsky-Sinn include:

1. The first homogeneous catalyst system with activity as high as conventional heterogeneous Ziegler-Natta systems.
2. These well-defined single site catalyst systems facilitate investigations of polymerization mechanism, which includes polymerization activity, relation between catalyst structure and polymer structure, etc.
3. Results in a better understanding of the polymerization mechanism and activity, allowing for design of new transition metal catalyst and synthesis of new polymers.
4. Most importantly, Kaminsky-Sinn catalyst has opened the door to new era of transition metal olefin coordination catalysts.

During the last two decades since discovery of the Kaminsky-Sinn catalysts, the development of transition metal olefin coordination catalysts have reached a new peak, and a lot of progress has been achieved.<sup>8,9</sup>

Some examples of Kaminsky-Sinn type catalysts, often called group 4 metallocene catalysts, are illustrated in Figure 3.2. The first homogeneous group 4 metallocene catalyst systems used large excess amounts of MAO to activate the catalyst and these system showed

high activity as compared to conventional heterogeneous systems. There are still ambiguous points as to the role of MAO, however, it is generally agreed that MAO alkylates the metal center and also abstracts an alkyl ligand from complex to allow monomer to coordinate to the resulting cation.<sup>9,10</sup> Later, it was clearly demonstrated that the cationic 14-electron complex (oxidation state +4) has high activity toward olefin polymerization. Evidence for this comes from the fact that same level of activity was obtained when noncoordinating bulky tetrakis(pentafluorophenyl)borate anion,  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , was used to activate alkyl species instead of MAO.<sup>10,11</sup>



**Figure 3.2:** Examples of metallocene catalysts

In propylene polymerizations, the relationship between the catalyst structures and the polymer structures have been well investigated.<sup>12</sup> Atactic polypropylene can be expected from achiral  $C_{2v}$  symmetric metallocene catalyst, Figure 3.2 (a). On the other hand, isotactic polypropylene and syndiotactic polypropylene can be obtained from chiral  $C_2$  symmetric metallocene catalysts, Figure 3.2 (b), and prochiral  $C_s$  symmetric *ansa*-metallocene catalyst, Figure 3.2 (c), respectively. Isotactic polypropylene is a highly crystalline polymer material,

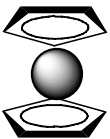
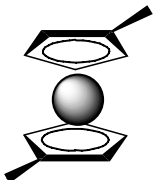
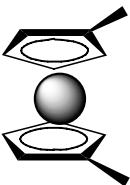
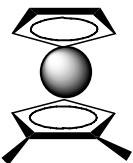
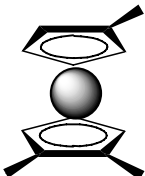
which also can be obtained from conventional heterogeneous Ziegler-Natta catalysts. However, syndiotactic polypropylene has never been synthesized until discovery of the metallocene catalysts.

Stereoselectivity during  $\alpha$ -olefin polymerizations, such as a propylene polymerization, is basically controlled by two mechanisms *enantiomorphic site control* and *chain end control*.<sup>1,12</sup> Ewen and his co-workers described a series of site control stereoselectivity rules based on several types of metallocene catalyst symmetries, Figure 3.3.<sup>13-17</sup> Site control can more strongly affect stereoselectivity than chain end control based on activation energy analysis. However, at low temperature, -15~-80°C, isospecific polypropylene polymerization can be observed with  $C_{2v}$  metallocene catalysts.<sup>14</sup> This isospecificity is due to chain end control.

Metallocene complexes in which the two cyclopentadienyl ligands are methylene-bridged are often called *ansa*-metallocene complexes. Not only does this methylene bridge prevent rotation of the ligands so as to prevent isomerization of complex, but it also forces the cyclopentadiene(Cp)-metal(M)-cyclopentadiene(Cp) angle to close more acutely. The more acute the Cp-M-Cp angle is, the more open coordination site is, and a monomer can approach to the metal center more readily.

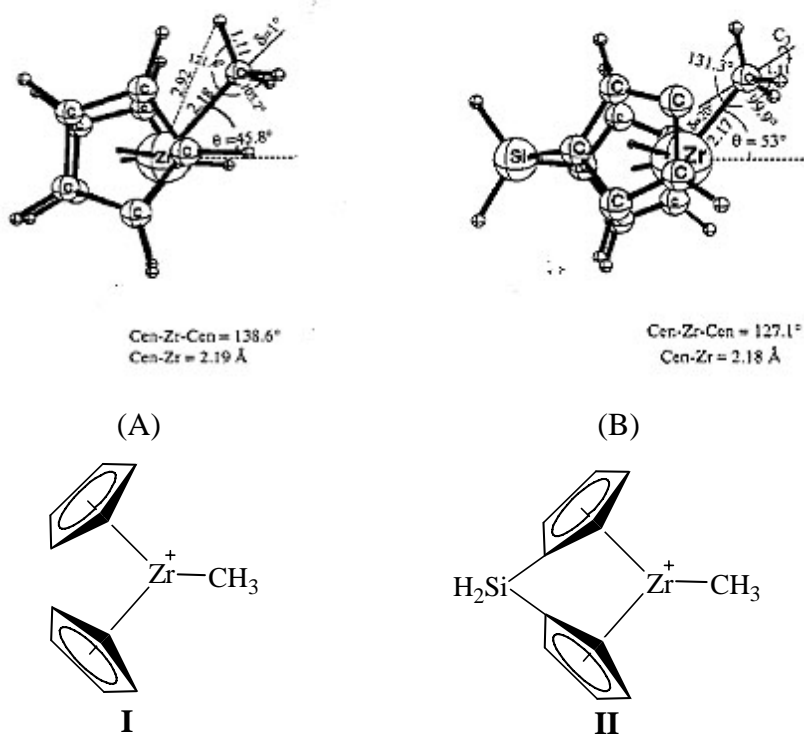
This wider coordination feature of the *ansa*-metallocene catalysts was suggested by density functional calculations.<sup>18</sup> Ziegler and his co-worker calculated the optimized geometries of and ethylene insertion barriers for cationic zirconocene **I** and cationic *ansa*-zirconocene **II**, Figure 3.4. According to their calculations, the optimized geometry of **II** has

a more open coordination site for the olefin than **I**, and insertion barrier for ethylene into **II** is 2.9 kcal/mol lower than that of **I**.

	Symmetry	Sites	Polymer
	$C_{2v}$ Achiral	A, A Homotopic	Atactic
	$C_2$ Chiral	E, E Homotopic	Isotactic
	$C_s$ Achiral	A, A Diastereotopic	Atactic
	$C_s$ Prochiral	E, -E Enantiotopic	Syndiotactic
	$C_1$ Chiral	E, A Diastereotopic	Hemi-isotactic

E=enantioselective site    A=nonselective site

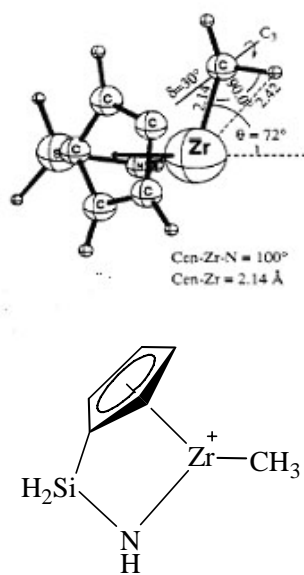
**Figure 3.3:** Relation between metallocene symmetry and tacticity



**Figure 3.4:** Optimized geometries of (A)  $\text{Cp}_2\text{ZrCH}_3^+$ , **I** and (B)  $\text{SiH}_2\text{Cp}_2\text{ZrCH}_3^+$ , **II**. (Reproduction from *Organometallics* **1994**, *13*, 2252)

For years now, an extensive amount of work on new metallocene catalysts research has been ongoing in many companies including the Dow Chemical Company. Dow researchers expanded on the concept of open coordination site further by replacing one Cp ring with an amido moiety, Figure 3.5.<sup>19</sup> These types of complexes are called “constrained geometry complex (catalyst)” or CGC, and are classified as a half-metallocene catalyst. Ziegler has also done calculation on CGC complexes and his calculations show that they have more open coordination sites for the olefin monomer.

The CGC possesses excellent catalytic activity toward  $\alpha$ -olefin polymerization, and under copolymerization conditions, using such monomer as ethylene and 1-hexene, the CGC

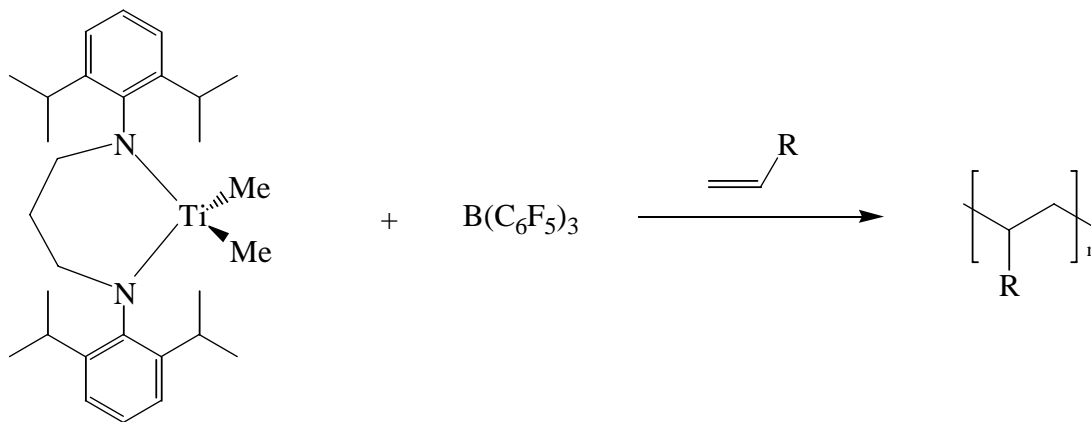


**Figure 3.5:** General structure of constrained geometry complex (cationic) and optimized geometry, where  $M=Zr$ ,  $R=R'=H$ . (Reproduction from *Organometallics* **1994**, *13*, 2252)

complexes shows high  $\alpha$ -olefin incorporation ratios.<sup>20,21</sup> This  $\alpha$ -olefin incorporation is a feasible catalytic characteristic presumably because of the wider coordination site. Another remarkable aspect of CGC catalyst is that CGC produces long-chain branched polyethylenes with narrow molecular weight distributions.<sup>22,23</sup>  $\beta$ -Hydride elimination and re-insertion are the source of the long-chain  $\alpha$ -olefins that become branches.<sup>24</sup> The discovery of constrained geometry catalyst (half-metallocene) triggered the search for new single site catalysts, which do not necessarily contain Cp rings.

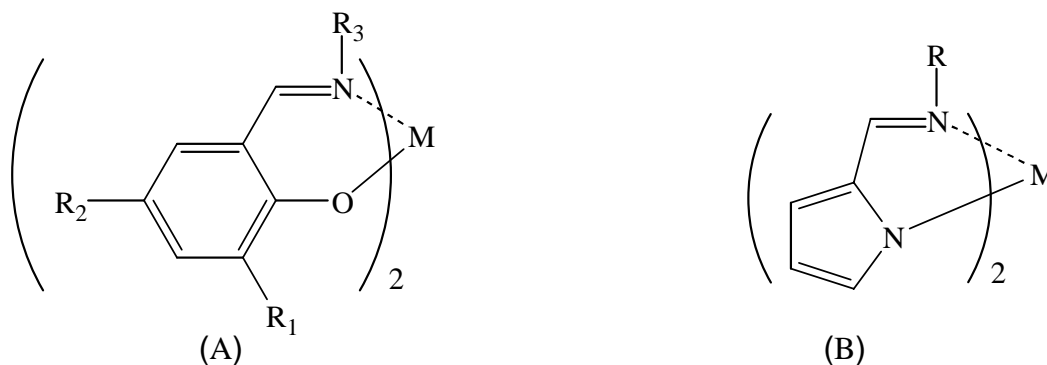
In 1996, McConville and his co-workers reported non-metallocene type diamide chelating titanium complexes that exhibit excellent catalytic activity toward  $\alpha$ -olefin polymerization in a living fashion, Scheme 3.2.<sup>25</sup>

**Scheme 3.2:** Diamide chelating Ti catalyst for  $\alpha$ -olefin polymerization.<sup>25</sup>



In 1998, a research group in Mitsui Chemicals published the first report of the family of group 4 metal catalysts bearing phenoxy-imine chelate ligands, Figure 3.6 (A).<sup>26</sup> The catalytic behavior and character depends on the activator and type of metal. These catalysts can be activated by MAO or trialkylaluminum/ $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ , and exhibit unique catalytic properties for polymerization of ethylene and/or  $\alpha$ -olefins, including higher  $\alpha$ -olefins and dienes.<sup>27</sup> In the case of zirconium, catalysts are capable of producing low molecular weight polyethylenes<sup>28</sup> and ultrahigh molecular weight ethylene/propylene copolymers with high activity.<sup>29</sup> In the titanium case, polymerization proceeds 2,1-insertion favored with 1-hexene and form high molecular weight atactic poly(1-hexene)s.<sup>30</sup> A fluorinated version of the titanium catalysts was found to catalyze ethylene and propylene polymerization in a living fashion even at high temperature, and a produced polypropylene is found to be highly syndiotactic.<sup>31-38</sup> Recently, Mitsui Chemicals research group reported similarly constructed

pyrrolide-imine titanium catalyst, Figure 3.6 (B).<sup>39,40</sup> This pyrrolide-imine type titanium catalyst polymerizes the cyclic monomer norbornene with ethylene in a living like fashion.

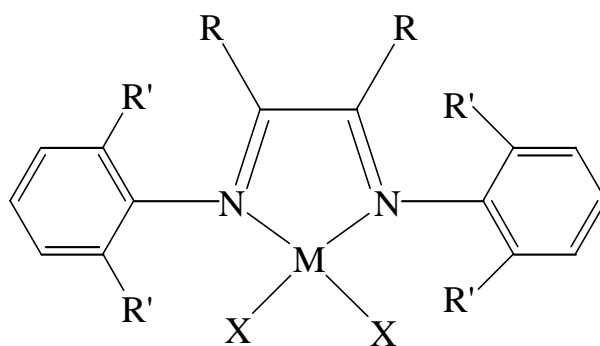


**Figure 3.6:** Mitsui Chemicals catalysts; (A) phenoxy-imine (R<sub>1</sub>, R<sub>2</sub> is alkyl group. R<sub>3</sub> is phenyl group. M is Ti, Zr or Hf.) (B) pyrrolide-imine (R is alkyl or phenyl group. M is Zr or Ti.)

Alternatively, iron, nickel and palladium, late transition metal complexes have also been investigated extensively as the post metallocene catalysts. The nature of late transition metals is the *d*-orbital energies lie relatively lower compared to early transition metals. Because of this low lying *d*-orbital energy, *d*-orbital in late transition metal accept electrons easily and low oxidation state complexes are readily formed. Typically, the electrons in the *d*-orbital make late transition metal catalyst systems display low polymerization activities and easy  $\beta$ -hydride eliminations because  $\pi$ -back donation makes the resulting  $\pi$ -complex stable, Figure 3.2. On the other hand, late transition metals are less oxophilic than early transition metals. Hence, late transition metal catalyst has a potential to polymerize monomers with wide variety of functional groups or in the presence of oxygen/water.

In 1995 Brookhart and his co-workers reported palladium and nickel based ethylene/ $\alpha$ -olefin polymerization catalysts, Figure 3.7.<sup>41,42</sup> Their catalyst system shows very

high catalytic activity toward ethylene polymerization. The special features of Brookhart catalysts is that nickel catalyst polymerizes  $\alpha$ -olefin in a living like fashion,<sup>43</sup> ethylene

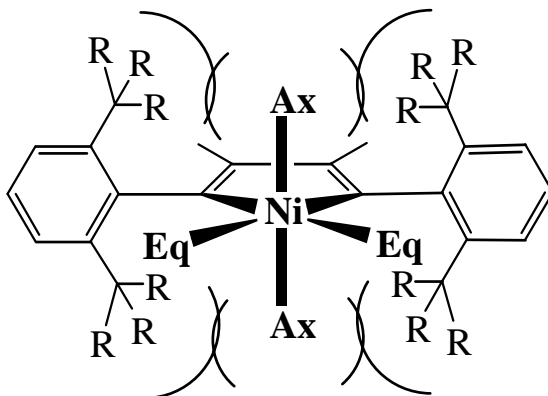


**Figure 3.7:** General structure of Brookhart nickel and palladium catalysts. (M=Ni or Pd, X=alkyl or halogen, R and R'=alkyl)

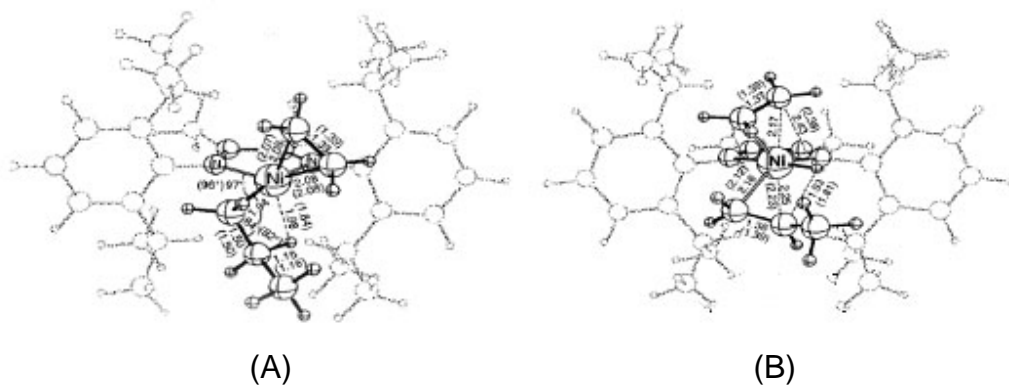
polymer from nickel catalyzed polymerization has short branches<sup>44</sup> and palladium catalyst can polymerize ethylene with methyl acrylate.<sup>45</sup>

Brookhart has suggested that the bulky aryl ligands act to preferentially block the axial sites of the metal center as illustrated by Figure 3.8.<sup>42</sup> A combined density functional theory and molecular mechanics studies of the nickel catalyst system has been performed by Ziegler and his co-workers.<sup>46</sup> According to their calculations, during polymerization, the olefin coordinated resting state and transition state for termination occupy the axial position and because of steric repulsion with bulky aryl ligands olefin coordinated resting state and

transition state for termination are dramatically destabilized, which results in a faster propagation rate and slower termination rate, Figure 3.9.



**Figure 3.8:** Steric interactions between bulky aryl ligands and axial coordination site of the metal center.

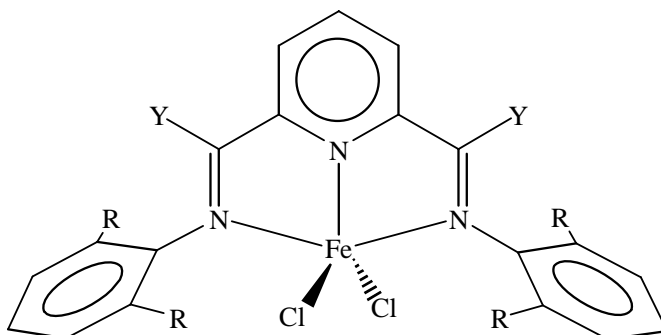


**Figure 3.9:** Optimized structures of resting state, (A) and transition state of termination, (B). Propyl metal cation and ethylene are used as model. (Reproduced from *J. Am. Chem. Soc.* **1997**, *119*, 6177)

Ethylene and methyl acrylate copolymerization catalyzed by palladium catalyst produce polyethylene with methacrylate terminated short branches. The ethylene homopolymerizations catalyzed by nickel catalyst produce short chain branches. Mechanistically, the formation of these two structural features are understood by same

phenomenon called “chain walking”.<sup>44,45</sup> In the copolymerization case, after 2,1-insertion of methyl acrylate catalyst center rearranges and forms an enolate which is inert toward further insertion, however, the palladium center “walks” down on polymer chain through series of  $\beta$ -hydride elimination-reinsertion steps then starts propagation again. As a result, methyl acrylate is always situated at the end of short branches. Similarly, in the case of ethylene homopolymerization by the nickel catalyst, the polymer chain bound to the nickel center does isomerizes by  $\beta$ -hydride elimination then migratory insertion occurs again.

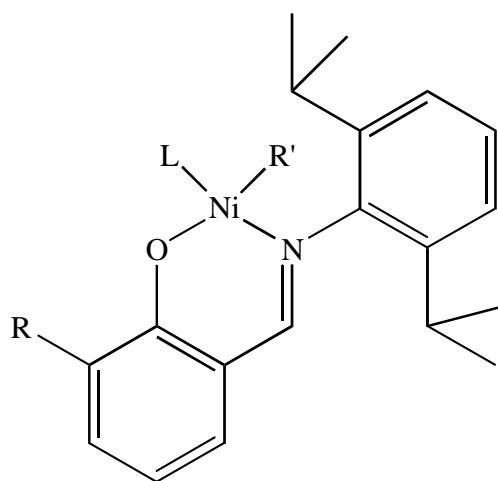
Remarkable work has also been done on iron catalyst systems worked on independently by Gibson and Brookhart. In 1999 they reported iron catalyst bearing tridentate pyridine  $\alpha$ -diimine ligand, of which general structure is illustrated by Figure 3.10.<sup>47-49</sup> Brookhart and Gibson iron catalyst system shows exceptionally high activity toward ethylene polymerization and isospecific polypropylene are obtained through chain end control with mainly 2,1-insetion mode.<sup>48</sup> Computational mechanism studies done by Ziegler suggests that the bulky imine aryl group has a similar role as in the case of nickel, which suppress ethylene capture for the termination step and increase the rate of insertion.<sup>50</sup>



Y=H,Me and R=t-Butyl, Iso-Propyl, etc.

**Figure 3.10:** Brookhart and Gibson iron catalyst for ethylene and  $\alpha$ -olefin polymerization.

The active species for all post metallocene catalyst systems shown above are all “cationic” species during polymerization, which are generated by a co-catalyst. In 2000 Grubbs and his co-workers reported first “neutral” nickel catalyst system that afford high molecular weight polymer for coordination-insertion polymerization, and which does not necessarily require to use co-catalyst, Figure 3.11.<sup>51-54</sup> Because of the less oxophilic character of nickel and the lack of charge on metal center, Grubbs nickel catalyst system is highly tolerant toward oxo-functional monomers such as norbornene derivatives.

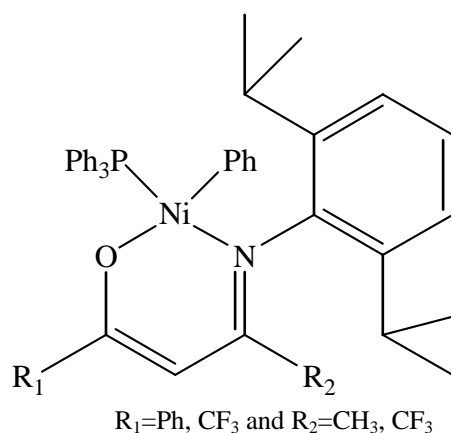


L=Ph<sub>3</sub>P, CH<sub>3</sub>CN, R=H,Ph, t-Butyl, etc. and R'=Ph, Me

**Figure 3.11:** Grubbs “neutral” nickel catalyst.

Random copolymerization of ethylene with polar functional olefin such as methyl acrylate has been adream for a long time. In 2005 a research group in China developed neutral nickel catalyst system that co-polymerizes ethylene and methyl methacrylate.<sup>55</sup> Figure 3.12 illustrates neutral nickel complex bearing  $\beta$ -ketoiminato chelate ligands. This neutral nickel complex activated by modified MAO exhibits high catalytic activity toward

ethylene with methyl methacrylate and produces high molecular weight functionalized polyethylene. Methyl methacrylate units are randomly built into the moderately branched polyethylene with close to 17 mol% of content.



**Figure 3.12:** Copolymerization neutral nickel catalyst for ethylene and methyl methacrylate.

The field of homogeneous single site coordination polymerization catalysts has made a great progress in the last two decades. These days, active catalysts are well-defined, mechanisms are well understood, and wide varieties of catalyst systems, early and late transition metal complexes, are available for various purposes, which include control of molecular weight, copolymerization with functional monomers,  $\alpha$ -olefin polymerization with or without stereocontrol and well-defined microstructures. Now we are able to utilize these various catalysts to create new class of materials.

## 3.2 Coordination-Insertion Polymerization of Cyclobutene

### 3.2.1 Polymerization of 1,2-Disubstituted Olefin

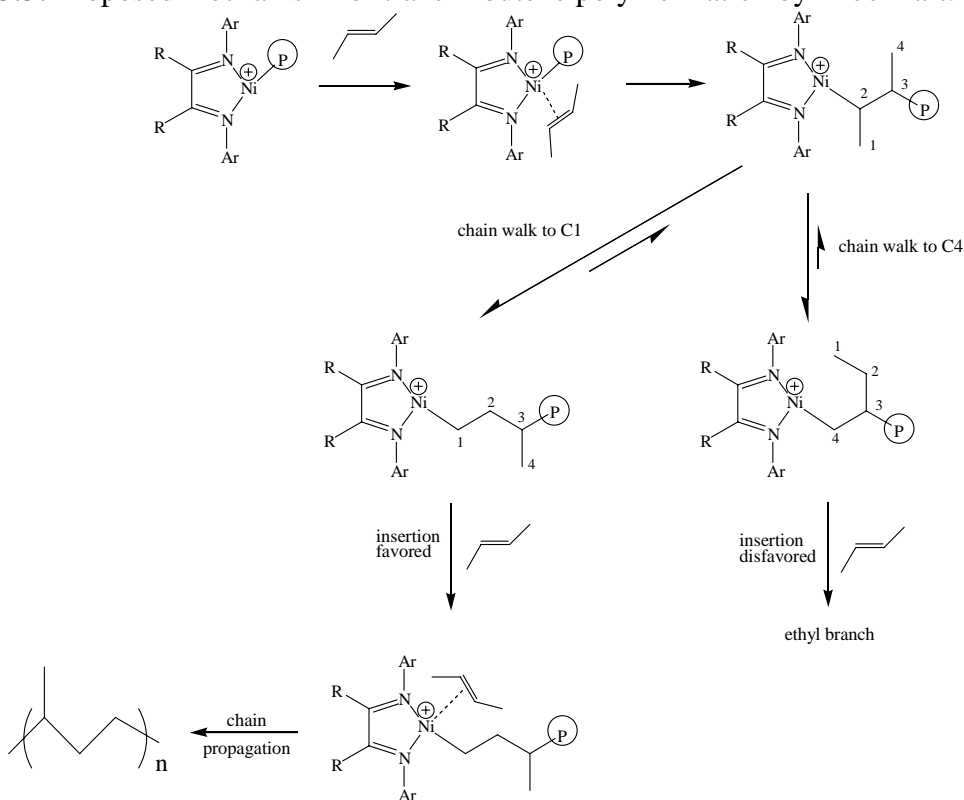
Transition metal catalysts for olefin polymerization have been developed to produce well-defined microstructures with interesting special properties from ethylene and  $\alpha$ -olefins. Although there has been considerable technological advancement of metal catalysts, the coordination polymerizations of internal olefins ( $\beta$ -olefins) still presents a challenge. These monomers known to produce low molecular weight homopolymers. This is due to the steric hindrance of the 1,2-disubstituted monomers around active metal center. Only a few examples coordination polymerization of  $\beta$ -olefin are known.

One relatively easy and compromised solution to polymerize  $\beta$ -olefins to high molecular weight polymers is to copolymerize the  $\beta$ -olefin with less steric bulk monomer like ethylene.<sup>56,57</sup> In this particular case, insertion of  $\beta$ -olefin to metal center takes place only after ethylene insertion to active center. This results in more than 50 mol% contents of ethylene incorporation into the copolymer.

Another solution is the monomer isomerization polymerization. Endo and his research group extensively have been investigating this method.<sup>58-63</sup> Internal olefin monomer like 2-butene is isomerized to terminal olefin in situ then isomerised monomer is subsequently subjected to polymerization. It is believed that two independent reactions are took place at different active site of metal center. This method provides direct one-pot polymerization of internal olefin, however, the problem is that it provides only 1-alkene polymer.

Recently, Brookhart reported direct polymerization of *trans*-2-butene catalyzed by nickel diimine complex.<sup>64,65</sup> It is revealed that *cis*-2-butene does not have an ability to insert and polymer from *trans*-2-butene has only methyl branches. Computational analysis by Cavallo suggest that *cis* isomer has higher insertion barrier than *trans* isomer.<sup>66</sup> Brookhart proposed the plausible mechanism for methyl branching from *trans*-2-butene polymerization, Scheme 3.3. After 2,3-insertion of every butene unit, active metal center chain walks so as to give methyl branches then propagation continues. In the case of chain walking in opposite direction does not lead to further insertions because of the steric repulsion between branching point and growing polymer chain. Methyl branch is precisely situated at every third carbon of the backbone.

**Scheme 3.3:** Proposed mechanism for *trans*-2-butene polymerization by Brookhart.



### 3.2.2 Polymerization of Cyclic Olefin

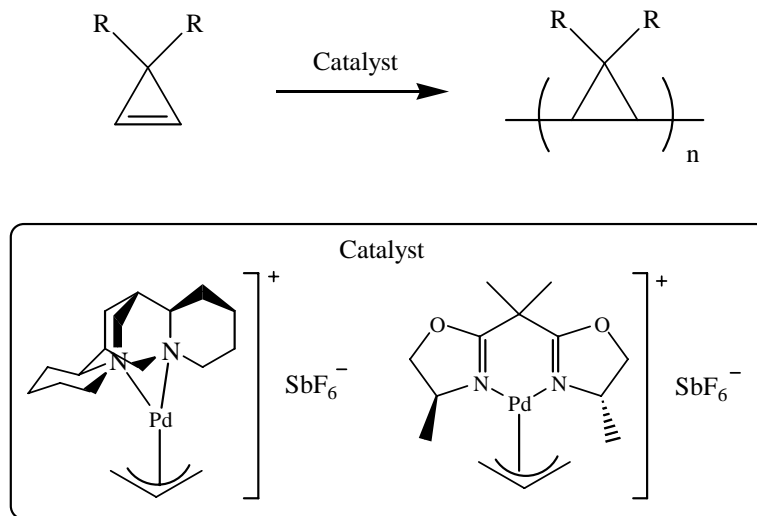
As stated, 1,2-disubstituted olefins cannot be polymerized or do so reluctantly. Although norbornene is a 1,2-disubstituted olefin, it is well known that norbornene polymerizes readily because of the release of ring strain energy contained within its bicyclic structure. One would anticipate that other strained cyclic olefins should also be active toward insertion polymerization and this is indeed the case. Norbornene has a ring strain of about 27 kcal/mol. This is comparable to the other strained olefins: cyclopropene, 55 kcal/mol, cyclobutene, 31 kcal/mol, cyclopentene, about 7 kcal/mol.<sup>67</sup> Cyclohexene, with a negligible ring strain of about 3 kcal/mol cannot be polymerized. Interestingly, of the 3, 4, and 5 membered rings, only the 3 and 5 membered rings have been successfully polymerized via an insertion mechanism.

In 1996, Risse and his co-workers reported addition polymerization of highly strained cyclopropene catalyzed by palladium complex. Due to the unstable nature of the unsubstituted cyclopropene, disubstituted cyclopropene unit was chosen, Scheme 3.4.<sup>68</sup> The cyclopropane unit and 1,2-cis enchainment was confirmed by NMR studies. Relative number and weight average molecular weights were  $M_n$  (GPC) = 42,000 and  $M_w$  (GPC) = 99,000, respectively.

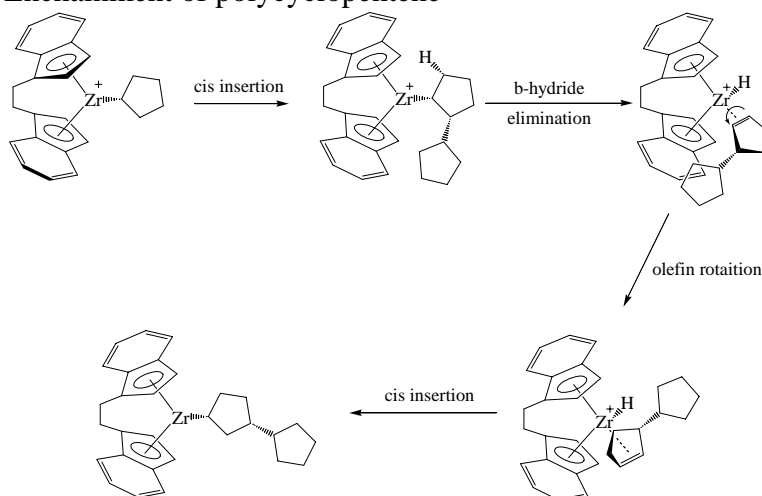
Kaminsky and his co-workers reported polymerization of cyclopentene using a heterogeneous catalyst system derived from zirconocene and MAO in 1989.<sup>69,70</sup> Polymerization proceeds without detectable ring opening of the monomer.<sup>71</sup> Highly crystalline isotactic polycyclopentene decomposes prior to melting in air and it is essentially insoluble to organic solvents. Solid-state  $^{13}\text{C}$ -NMR data was used to assign the

microstructure. They concluded that most of the polymer was formed by 1,2-enchainment and cis and trans stereochemistry were involved. However, it seems unlikely since the mechanism of Ziegler-Natta catalyst polymerization invariably involves cis insertion.

**Scheme 3.4:** Coordination-Insertion polymerization of cyclopropene derivatives.



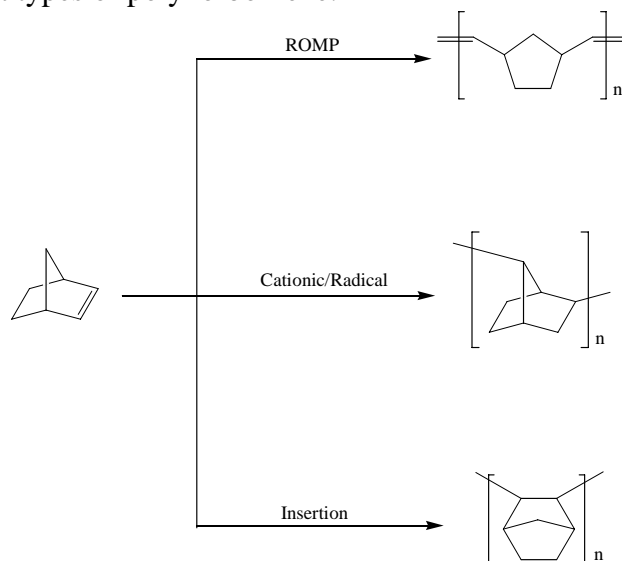
**Scheme 3.5:** 1,3-Enchainment of polycyclopentene



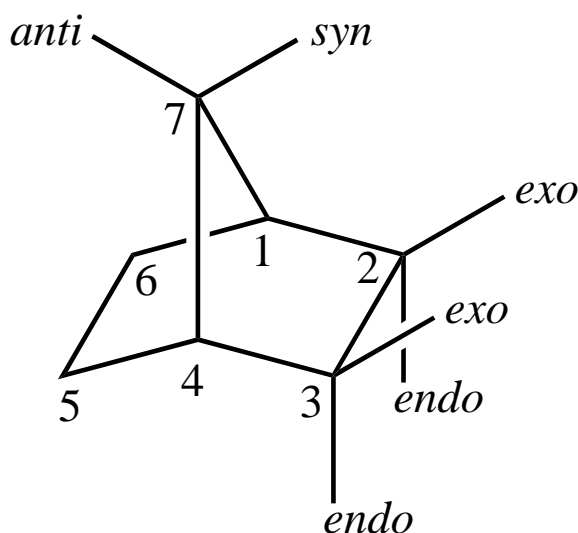
A series of studies conducted by Collins reveals the real structure of polycyclopentene obtained from reactions catalyzed by homogeneous zirconocene catalysts.<sup>72-74</sup> According to their analysis of ligomers, polycyclopentene has predominantly cis 1,3-enchainment. It is implied that reversible  $\beta$ -hydride elimination mechanism accounts for 1,3-enchainment propagation reaction to avoid steric bulk between incoming monomer unit and growing polymer chain, Scheme 3.5. Brookhart and Du Pont research group also suggested cis 1,3-enchainment of polycyclopentene from nickel and palladium catalyzed polymerization.<sup>75</sup>

Norbornene, bicyclo[2.2.1]hept-2-ene, has been polymerized with variety of catalysts. The ring opening metathesis polymerization<sup>76</sup> is the best known of three different types of norbornene polymerization, Scheme 3.6. The vinyl polymerization of norbornene has also been the subject of a number of studies,<sup>77</sup> but only a few cases of radical /cationic polymerization have been reported.<sup>78</sup>

**Scheme 3.6:** Different types of polynorbornene.



Many coordination-insertion polymerizations of norbornene mediated by transition metal catalysts are well known and documented.<sup>79</sup> Group 4 metallocene catalysts in combination with MAO promote the vinyl polymerization<sup>79,80</sup> as well as  $L_2PdX_2$  type catalysts which can even tolerate functional groups.<sup>78,81,82</sup> It is suggested that both early- and late-transition metal catalyzed polymerization promote *cis-exo* insertion of norbornene unit, Figure 3.13.<sup>80,83-86</sup>

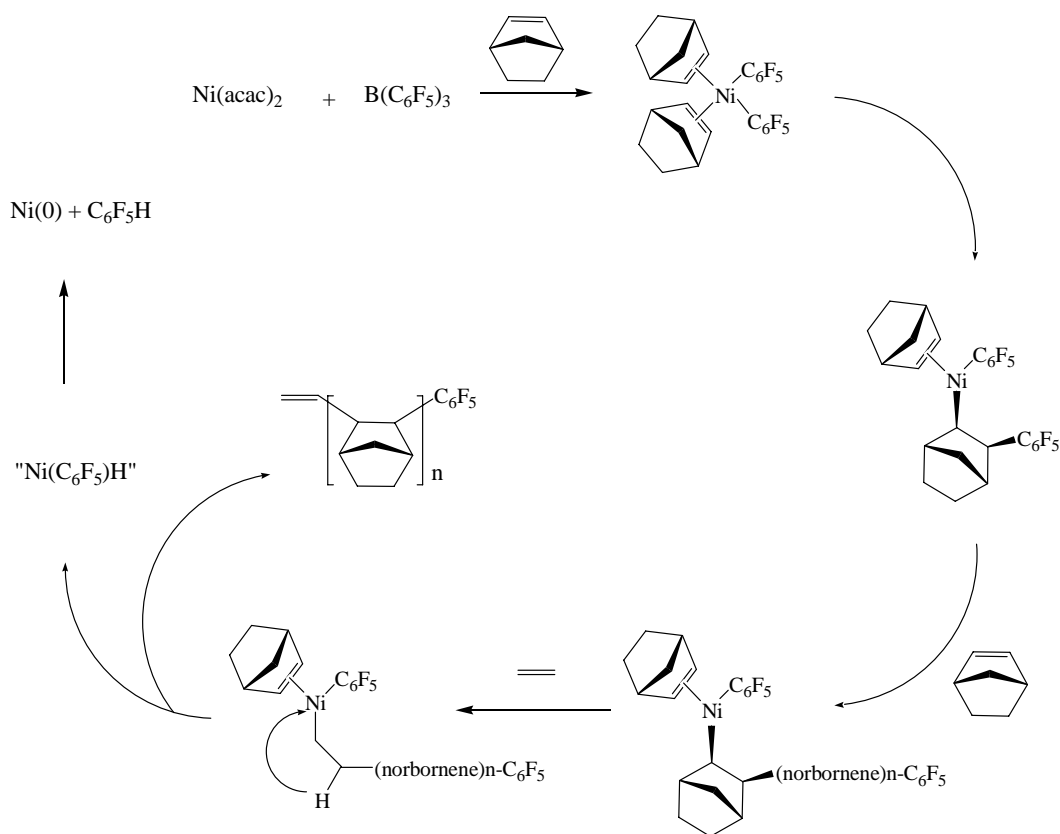


**Figure 3.13:** Stereochemical orientations and numbering in a norbornene.

An important feature of norbornene as a monomer for coordination polymerization opposed to most of other monomers is a lack of an ability of  $\beta$ -hydride elimination. One available hydrogen for  $\beta$ -hydride elimination is situated on the bridgehead carbon, C-4 (C-1) in Figure 3.13, but a bridge-head double bond is prohibited by Bredt's rule. In addition to this, it is widely accepted that an in-plane  $\beta$ -agostic complex forms prior to  $\beta$ -hydride elimination.

However, the relative positions of the metal center and  $\beta$ -hydrogen, either C-4 (C-1) or C-2 (C-3), is not sufficient to have good orbital overlap.<sup>18,46,87,88</sup>

Risse and his co-worker reported polymerization of norbornene and its derivatives catalyzed by  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ <sup>81,82,89</sup>, while Goodall and his co-workers reported nickel catalyzed polymerization, Figure 3.14.<sup>86,90</sup>

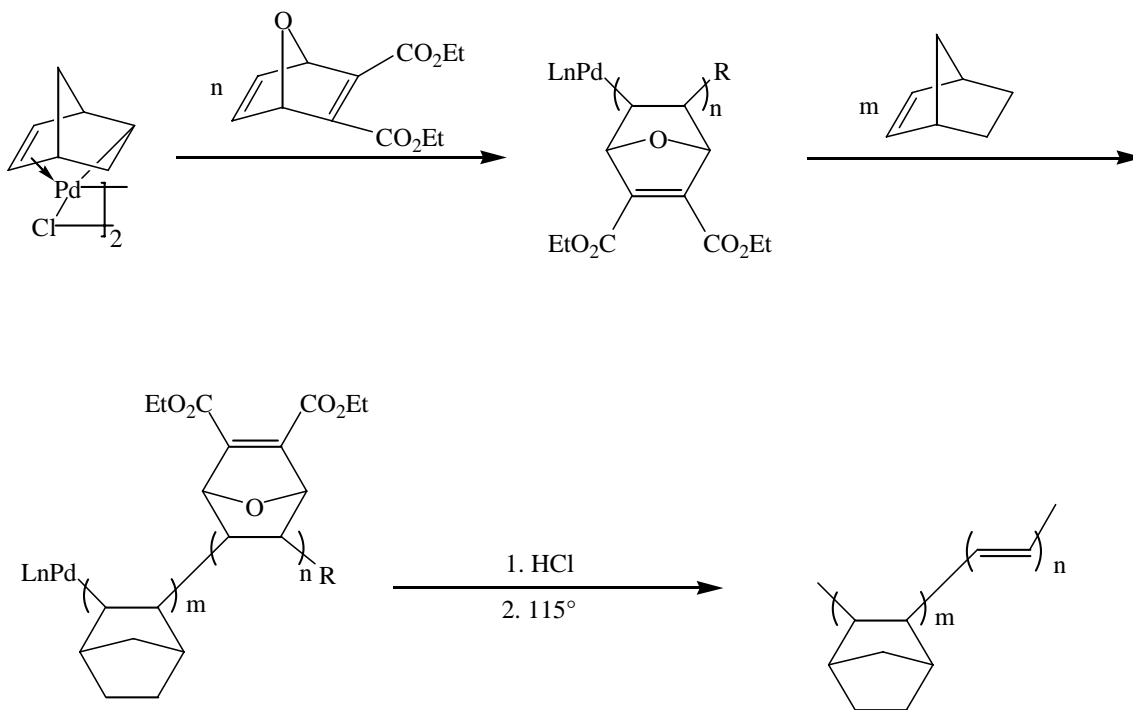


**Figure 3.14:** Simple nickel complex catalyzed norbornene polymerization.<sup>86,90</sup>

In our research group, a series of the  $\sigma$ ,  $\pi$ -bicyclic chelating ligand palladium catalysts for living polymerization of norbornene have been developed, and one example is

shown in Scheme 3.7.<sup>91</sup> Polymerization proceeds in living fashion and oxy-functional group does not prevent polymerizations. All the cyclic structures are preserved through polymerization, and even the easy retro-Diels-Alder reaction does not take place. The most interesting aspect of this polymerization is the stability of the palladium centers. Not only are these types of initiators air and moisture stable and thus suitable for bench top polymerizations (those catalysts are all atmospherically stable for more than 12 h, and no variations are observed when the polymerizations are conducted under an inert atmosphere) but they also remain active at the chain ends, even after isolation and storage in the solid state. These “polymeric reagents” can be used for the preparation of block copolymers by dissolving them in a solution containing the second monomer, Scheme 3.7.

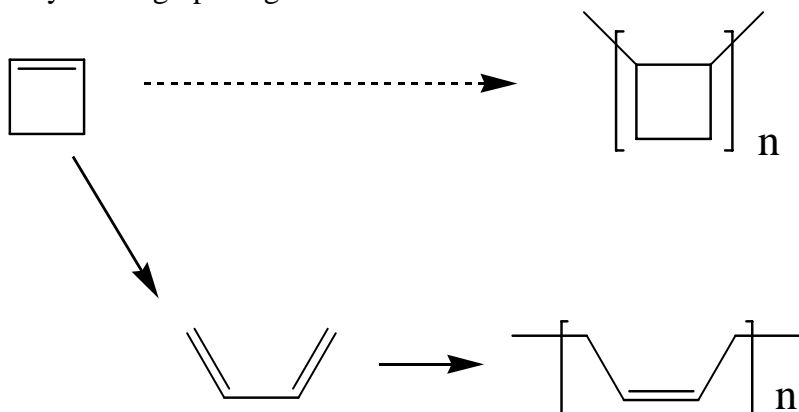
**Scheme 3.7:** Living polymerization of norbornene and its oxy-functionalized derivative by palladium initiator.<sup>91</sup>



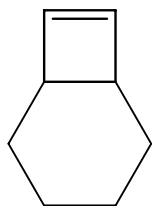
### 3.2.3 Cyclobutene Polymerization

Although cyclobutene has sufficient ring strain, 31 kcal/mol, very few examples of vinylic polymerization of cyclobutene are known. Polymerization of the 4 membered ring, although highly strained, has been less successful. This is due to the fact that simple cyclobutenes will undergo rapid pericyclic ring opening reactions to form butadiene. Attempts to polymerize cyclobutene results in a polymer that contain both the cyclobutene repeats and 1,4-butadiene repeat units, Scheme 3.8. These butadiene repeats destroy the thermostability of the polymer.<sup>92</sup>

**Scheme 3.8:** Pericyclic ring opening reaction of butadiene.



In 1960s, Dall'asta and his co-workers reported several publications of polymerization of cyclobutene, however their polymer contains butadiene units and ring opening polymerization units. Also molecular weight information is obscure.<sup>92-94</sup> They also tried to polymerize the fused ring system, bicyclo[4.2.0]oct-7-ene and bicyclo[3.2.0]hepta-2,6-diene, Figure 3.15. Resulting polymer has quite small molecular weights, such as 1,000, and contains ring opening units up to 10 % mol, Scheme 3.9.<sup>95</sup>



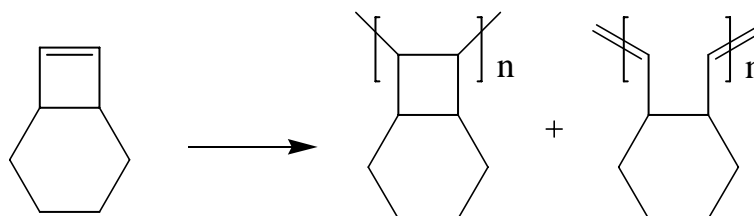
bicyclo[4.2.0]oct-7-ene



bicyclo[3.2.0]hepta-2,6-diene

**Figure 3.15:** Fused ring cyclobutene monomers.

**Scheme 3.9:** Polymer has very low molecular weight and ROMP structure.



To the best of our knowledge, no reports of high molecular weight, genuine vinylic polymer of any cyclobutene derivatives have been published.

### 3.2.4 New Monomer

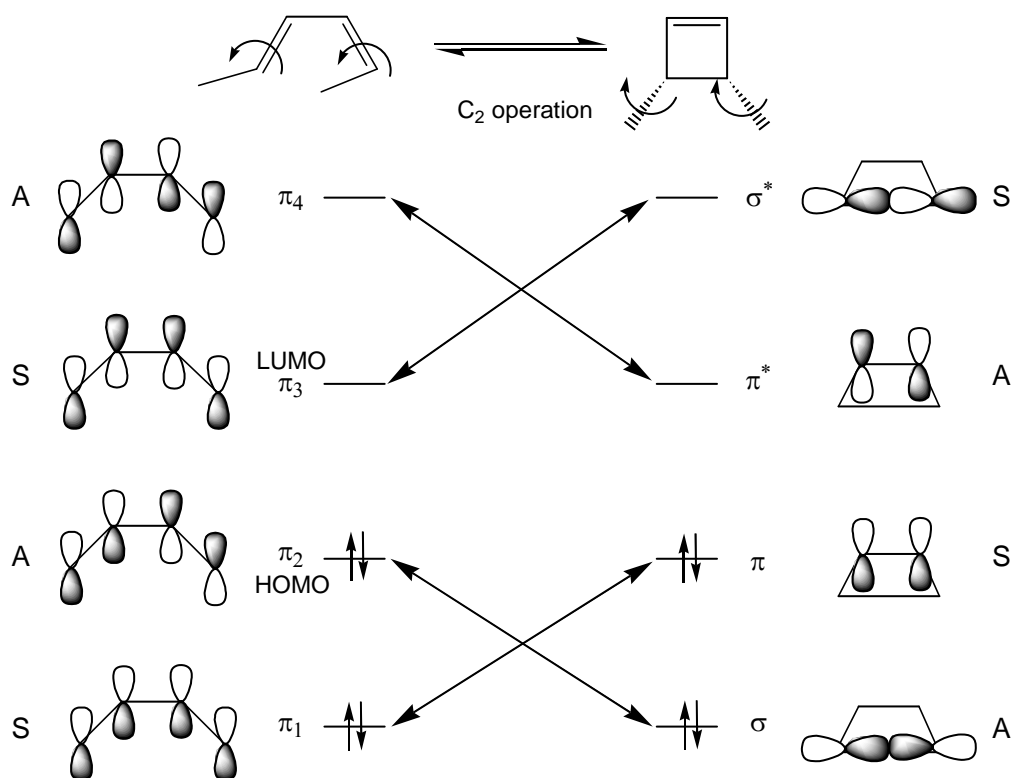
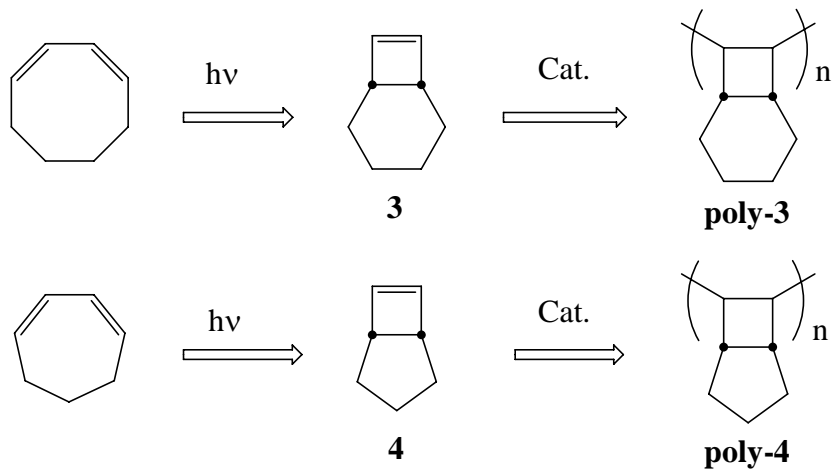
In recent years a number of new high performance engineering materials have been prepared through the insertion polymerization of norbornene. These polymers can have outstanding properties, such as low moisture absorption, low dielectric constants, chemical resistance, low birefringence, high breakdown voltages and high glass transition temperatures. A number of those polynorbornene materials are now commercially available and include *Appear*® optical polymer material for flat panel display and waveguides, *Aprima*® adhesives and cover-coat, *Avatrel*® low-κ materials, *Duvcor*® 193 nm and 157 nm photoresists

(Promerus spin-off from BFGoodrich), as well as copolymer of olefins and norbornenes, *Topas*® (Topas Advanced Polymers) and *Apel* ® (Mitsui Chemical). Since many frontier work of polynorbornene research has been done in industry, the patent fence protects materials containing the norbornene ring system is formidable.

As stated earlier, the insertion polymerization of the 4-membered ring, although highly strained, has been less successful. The unwanted pericyclic ring-opening of cyclobutene to the more stable butadiene problem has left the cyclobutene field wide open in terms of new materials developed. Hence, successfully eliminating this pericyclic reaction that forms butadiene will allow for the development of a whole family of new polymers. We anticipate these materials to have properties comparable to the polynorbornenes; high glass transition temperatures, very high transparencies, low moisture uptake, etc.

Our approach to eliminating the pericyclic ring opening reaction will be to tie the 3, 4-carbons of the butadiene together through an additional fused ring. This “cis” fused ring prevents the facile pericyclic ring opening from occurring, bicyclo[4.2.0]oct-7-ene (**3**) and bicyclo[3.2.0]hept-6-ene (**4**), Scheme 3.10. Pericyclic ring opening is thermally forbidden process for cis,cis configuration, Figure 3.16.<sup>96</sup>

**Scheme 3.10:** Our new monomers.













**Figure 3.16:** Thermally allowed conrotatory orbital correlation diagram.

### 3.3 Ring Strain

#### 3.3.1 Evaluation of Ring Strain (Calculation Method)

As discussed, the polymerization of 1,2-disubstituted olefins is not polymerizable because of steric hindrance. To overcome this steric hindrance, we can utilize the ring strain contained in fused ring olefin systems. The ring strain energies data for cyclic olefins and their parents cyclic hydrocarbon compounds are listed in Table 3.1.<sup>67,97</sup>

**Table 3.1:** Strain energies based on experimentally determined heats of formation.<sup>67</sup>

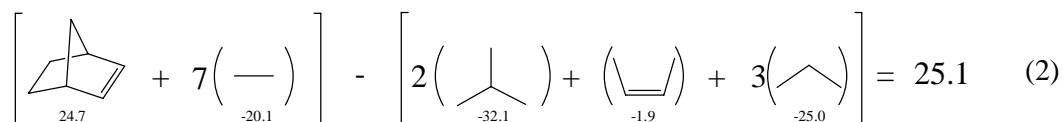
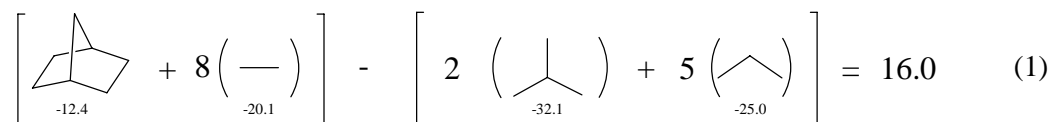
	Strain Energy (kcal/mol)
	28.1
	54.5
Difference (Olefin Strain)	26.4
	26.9
	30.6
Difference (Olefin Strain)	3.7
	7.2
	6.8
Difference (Olefin Strain)	-0.4
	1.4
	2.5
Difference (Olefin Strain)	1.1
	17.6
	27.2
Difference (Olefin Strain)	9.6

Among them cyclopropene and norbornene are known to polymerize readily to afford high molecular weight polymer. Feasibility of polymerization of cyclic olefin relies on its ring strain, in detail; it relies on strain energy difference between monomer and repeating unit. In the cases of norbornene and cyclopropene, those numbers are approximately 10 kcal/mol and 26 kcal/mol, respectively. Cyclobutene, which is known to give only oligomers with ring opening side reactions, has only 3.7 kcal/mol difference between monomer and repeat, even ring strain energies are quite high. Cyclohexene, which is known notoriously not polymerizable, has only 1 kcal/mol difference. Surprisingly, cyclopentene, which is recently reported polymerizable through 1,3-enchainment, has a negative value. From these data and except for cyclopentene case, strain energy difference between olefin monomer and repeating unit for polymerizable monomer is deduced to be higher than 10 kcal/mol.

The ring strain energy of a molecule can be calculated from its heat of formation. Once the heat of formation is determined, ideally by experiment, one can calculate ring strain energy by comparison to its hypothetical “strain-free” model.<sup>97,98</sup>

For example, ring strain energies of norbornene and norbornane are calculated in eqs. (1) and (2). Heats of formation of norbornene and norbornane are referred from Schleyer literature<sup>67</sup> and some example values are listed in Table 3.2.<sup>99</sup> Although there is little deviation from literature data, numbers calculated in this fashion are in good accordance with the experimental values. In the calculations shown in equations 1 and 2, we do not employ any error correction method that is sometimes employed literatures,<sup>67,97,98,100</sup> therefore our numbers may contain some additional error value. However, for evaluation of ring strain

energy differences, we assume that this calculation method gives us an appropriate idea and is useful for all practical purposes.



**Table 3.2:** Heats of formation of small molecules.<sup>99</sup>

Element	Heat of Formation (Kcal/mol)
Ethane	-20.1±0.05
Iso-Butane	-32.1±0.1
(Z)-Butene	-1.9±0.1
(E)-Butene	-2.9±0.2
Propane	-25.0±0.1
Ethylene	12.5±0.2
Propylene	4.8±0.2

### 3.3.2 Ring Strain of New Monomers (Comparison with Norbornene)

Ring strain energies of proposed new monomers, bicyclo[4.2.0]oct-7-ene (**3**) and bicyclo[3.2.0]hept-6-ene (**4**), were calculated. Based on the reported value of heats of formations<sup>67,100,101</sup> and values listed on Table 3.2. Simple additions of those values in conformity with equations 3, 4, 5, and 6 provide ring strain energies. Strain energy difference between monomer and repeating unit is 11.1 kcal/mol and 5.5 kcal/mol for **3** and **4**, respectively. Norbornene has about 10 kcal/mol difference and it is polymerizable through addition polymerization. These results encouraged us to investigate these monomers further.

$$\left[ \begin{array}{c} \text{Bicyclo[4.2.0]oct-7-ene} \\ -6.1 \end{array} + 9 \left( \text{Ethylene} \right)_{-20.1} \right] - \left[ 2 \left( \text{Isobutylene} \right)_{-32.1} + 6 \left( \text{Propene} \right)_{-25.0} \right] = 27.2 \quad (3)$$

$$\left[ \begin{array}{c} \text{Bicyclo[4.2.0]oct-7-ene} \\ 33 \\ \mathbf{3} \end{array} + 8 \left( \text{Ethylene} \right)_{-20.1} \right] - \left[ 2 \left( \text{Isobutylene} \right)_{-32.1} + \left( \text{Vinylcyclopropane} \right)_{-1.9} + 4 \left( \text{Propene} \right)_{-25.0} \right] = 38.3 \quad (4)$$

$$\left[ \begin{array}{c} \text{Bicyclo[3.2.0]hept-6-ene} \\ 4.5 \end{array} + 8 \left( \text{Ethylene} \right)_{-20.1} \right] - \left[ 2 \left( \text{Isobutylene} \right)_{-32.1} + 5 \left( \text{Propene} \right)_{-25.0} \right] = 32.9 \quad (5)$$

$$\left[ \begin{array}{c} \text{Bicyclo[3.2.0]hept-6-ene} \\ 38 \\ \mathbf{4} \end{array} + 7 \left( \text{Ethylene} \right)_{-20.1} \right] - \left[ 2 \left( \text{Isobutylene} \right)_{-32.1} + \left( \text{Vinylcyclopropane} \right)_{-1.9} + 3 \left( \text{Propene} \right)_{-25.0} \right] = 38.4 \quad (6)$$

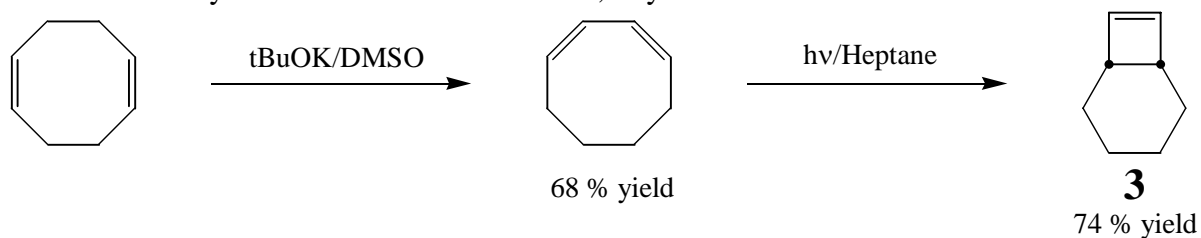
### 3.4 Preparation of New Monomers

The synthesis of monomer **3** and **4** is summarized in Scheme 3.11 and Scheme 3.12, respectively. All the steps are quite straightforward and in reasonable yields. (Yield percentages indicated are after purification.)

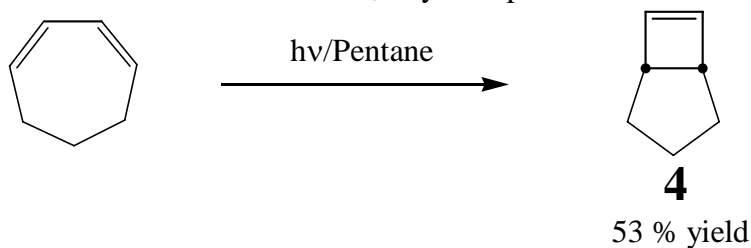
In the case of synthesis of monomer **3**, we started with 1,5-cyclooctadiene because of cost efficiency and availability. After base catalyzed isomerization to more thermally stable 1,3-cyclooctadiene isomer, photochemical transformation afforded monomer **3**.

To prepare monomer **4**, we first tried the synthesis starting with 1,3,5-heptatriene as starting material because of availability and economic reasons. Selective reduction of one double bond in 1,3,5-heptatriene can be found in literature.<sup>102</sup> However, the selectivity was not so good and purification was not particularly successful. We then decided to use 1,3-cycloheptadiene to synthesize monomer **4**. Because of availability and cost of 1,3-heptadiene, only limited amount of monomer **4** was synthesized.

**Scheme 3.11:** Synthesis of monomer **3** from 1,5-cyclooctadiene.

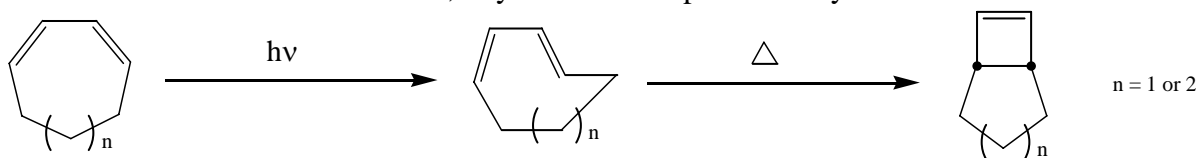


**Scheme 3.12:** Synthesis of monomer **4** from 1,3-cycloheptadiene.



As we expected the photochemical reactions for both 1,3-octadiene and 1,3-heptadiene gave the fused ring cyclobutene compounds.<sup>103-105</sup> However, to our surprise, according to literatures, both reactions proceed through isomerization of the cis, cis-isomer to highly strained cis, trans-isomer followed by thermal conrotatory cyclization, Scheme 3.13.<sup>104,105</sup>

**Scheme 3.13:** Transformation of 1,3-cyclodiene compounds to cyclobutene.



When the temperature of the reaction of 1,3-cyclooctadiene was not kept over 80°C, the reaction yield was quite low. This is consistent with the literature that says temperatures higher than 80°C are required for thermal cyclization reaction of cis, trans-1,3-cyclooctadiene.<sup>105</sup> On the other hand, the cis, trans-1,3-cycloheptadiene does not require such high temperature.<sup>104</sup>

Because of our limited supply of monomer **4**, we mainly focused on monomer **3** through our project.

### 3.5 Polymerization Studies

#### 3.5.1 Choice of Catalyst Systems

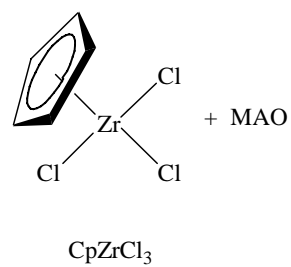
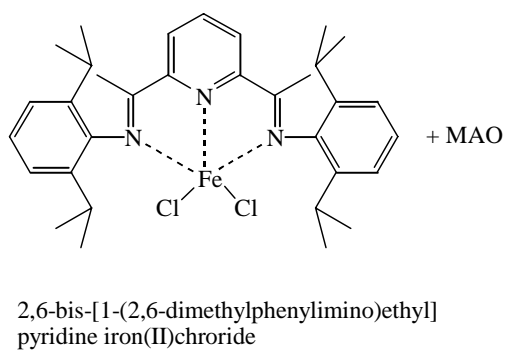
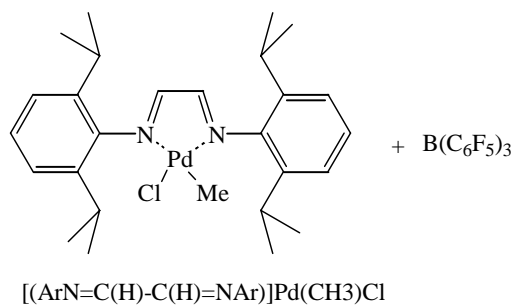
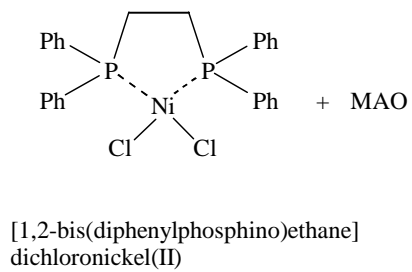
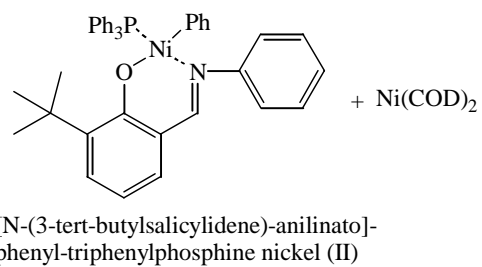
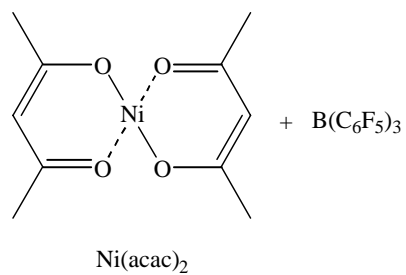
Since our monomers have fused ring systems similar to norbornene, it was assumed that  $\beta$ -hydride elimination would not be a significant process during polymerization. Late transition metal catalysts are prone to  $\beta$ -hydride eliminate unless bulky ligands are used, such as those in the Brookhart type nickel or palladium catalysts. For monomers like norbornene that don't have the intrinsic ability to  $\beta$ -hydride eliminate, simple nickel or palladium complex can be very active catalyst system.<sup>79</sup> Among the late transition metal catalyst systems, nickel(acetylacetonate) or its derivative with tris(pentafluorophenyl)borane system is simple yet shows high activity toward norbornene polymerization.<sup>90,106</sup> Another simple nickel catalyst system active for norbornene polymerization is [1,2-bis(diphenylphosphino)ethane]dichloronickel with MAO. This catalyst system first reported for ethylene polymerization in 1993,<sup>106</sup> and when we started this research there was no report about activity of this system toward norbornene polymerization. However, very recently Janiak and his co-workers reported that this system shows good polymerization activity toward norbornene.<sup>107</sup>

While these simple nickel complexes work very well toward the polymerization of norbornene, nickel or palladium complexes with well designed bulky ligand such as Grubbs type, salicylaldiminate neutral nickel catalyst system<sup>54</sup> or Brookhart type,  $\alpha$ -diimine palladium cationic catalyst system are also reported to be active toward norbornene/functionalized norbornene and ethylene co-polymerization.<sup>108,109</sup>

In contrast, early transition metal catalysts based on, titanium or zirconium, are known to have less of a tendency to  $\beta$ -hydride eliminate. However, titanium complexes, such as biscyclopentadienyl titanium for instance, is known to catalyze ring opening metathesis polymerization of norbornene as well.<sup>110</sup> In contrast, biscyclopentadienyl zirconium catalyzes exclusively addition polymerization of norbornene.<sup>110,111</sup> Because of steric repulsion, biscyclopentadienyl zirconium does not show high catalytic activity toward norbornene and a more open form of zirconocene would be better suited for strained cyclic olefin such as norbornene.

The Brookhart/Gibson type iron cationic catalyst systems are other good examples of well-designed and highly active catalyst system for olefin polymerization.<sup>47,49</sup> Although there is a report that this type of iron complex does not have activity toward norbornene,<sup>112</sup> its general high catalytic activity still hold our attention.

With all of these considerations, we mainly focused on nickel catalyst systems for preliminary polymerization study of monomer **3**. All six catalyst systems chosen are listed in Figure 3.17.

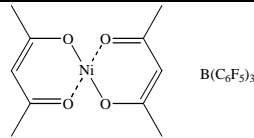
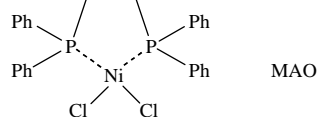
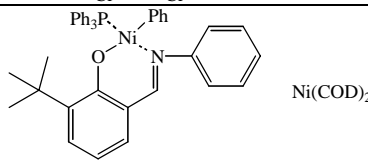
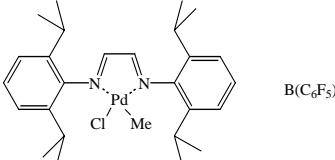
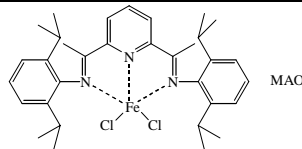
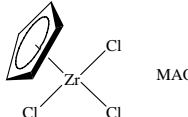


**Figure 3.17:** Catalyst systems for preliminary polymerization studies.

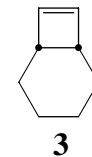
### 3.5.2 Result from Preliminary Polymerization Studies

The preliminary attempts to polymerize monomer **3** with various catalyst systems are summarize in Table 3.3.

**Table 3.3:** Polymerization Results of monomer **3** with various catalyst systems.

Run	Catalyst System	Yield (%)	Note
1	 $\text{B}(\text{C}_6\text{F}_5)_3$	0	-
2	 MAO	trace	-
3	 $\text{Ni}(\text{COD})_2$	0	-
4	 $\text{B}(\text{C}_6\text{F}_5)_3$	0	-
5	 MAO	trace	-
6	 MAO	50	Soluble in 1,2-dichlorobenzene Olefinic proton (NMR)

\*At room temperature and 24 hours reaction time. See the experimental section for detailed conditions.



Surprisingly, none of those late transition metal catalyst systems that are active toward norbornene showed activity toward monomer **3**, run 1 ~ 4. The iron catalyst system

didn't show any activity toward **3** either, run 5. Only cyclopentadienyl zirconium trichloride showed activity, which yielded 50 % of the polymeric product.

Generally high molecular weight polynorbornene is not soluble in organic solvents at least at room temperature. Since polymeric product from polymerization of **3** catalyzed by cyclopentadienyl zirconium trichloride is soluble to 1,2-dichlorobenzene and partially soluble to toluene and chloroform, we assumed that this product had a low molecular weight. Signals for olefinic protons were found using NMR spectrum, and gel permeation chromatography showed a trimodal polymer distribution from high molecular weight region to low molecular weight region. Polymerization seemed to proceed through multiple active centers; hence the trimodal distribution.

### ***3.5.3 Origin of Olefin Structure***

We thought of three possible origins of olefin peaks present in the NMR and we tried to prove which hypothesis is the most reasonable.

- (1) Ring Opening Metathesis Polymerization.
- (2) Thermal transformation of **3** to 1,3-cyclooctadiene followed by 1,2- or 1,4-enchainment polymerization.
- (3)  $\beta$ -Hydride elimination.

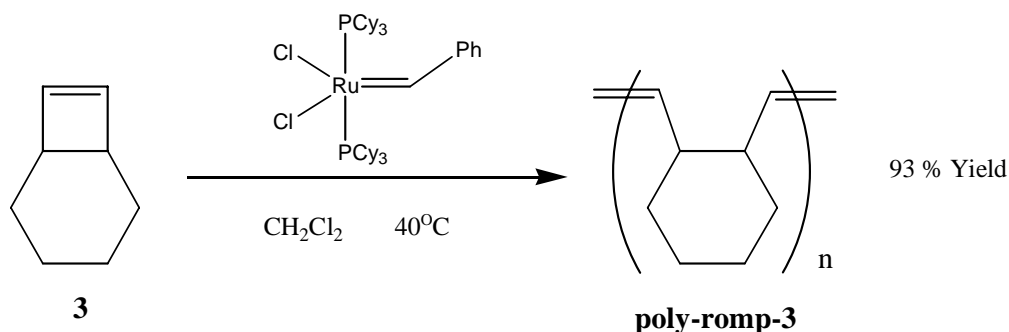
#### **(1) Ring Opening Metathesis Polymerization**

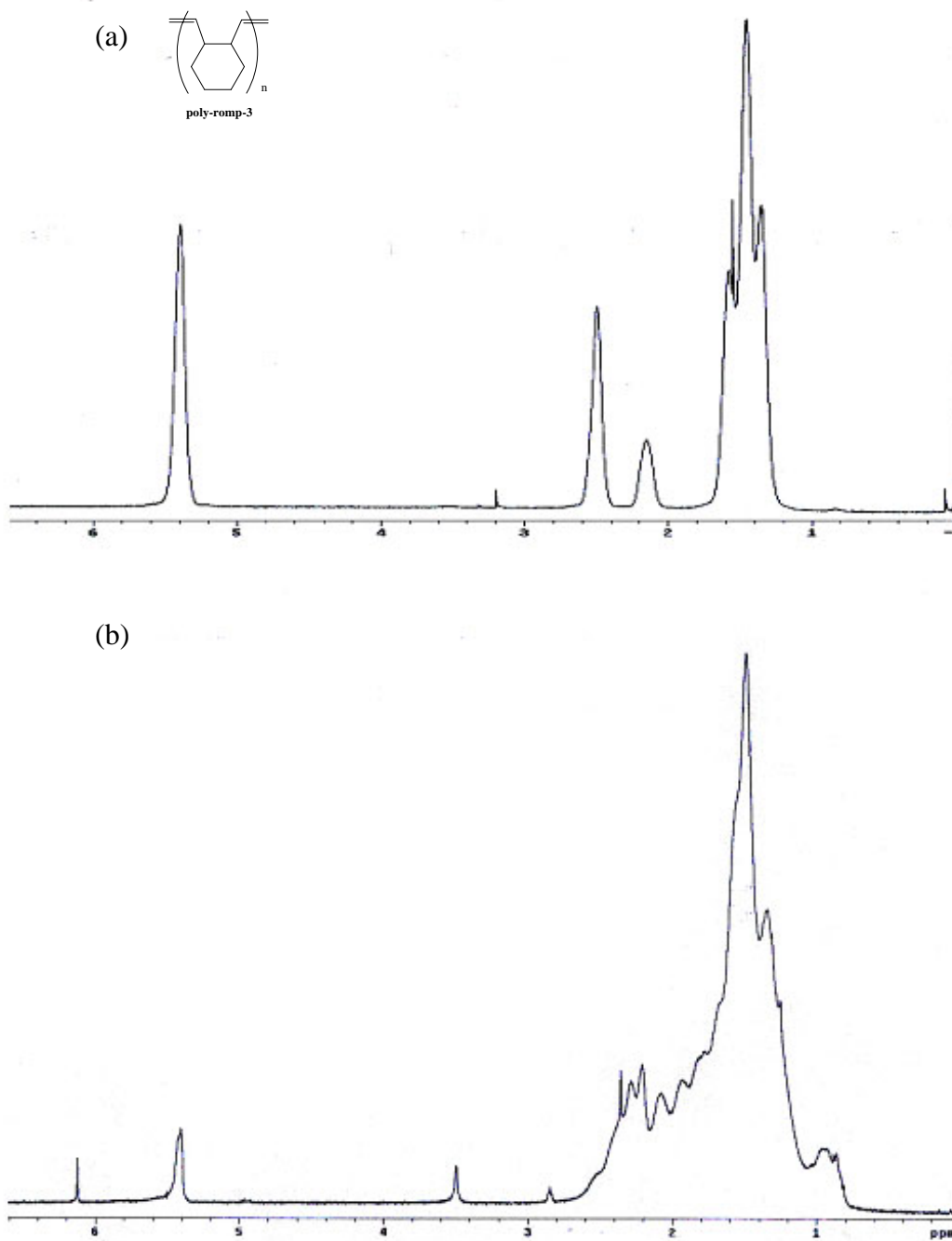
Although it is known that zirconium does not catalyze ROMP, we conducted the following control experiments. ROMP polymer of **3** was synthesized catalyzed by using

Grubbs' ruthenium catalyst, Scheme 3.14. The  $^1\text{H}$ -NMR spectra of these two polymers were different from one another overall, however, the chemical shift of olefin proton of each spectrum are same, 5.4 ppm, Figure 3.18. So we then conducted another experiment.

Osmium tetroxide with periodic acid is known to cleave carbon-carbon double bonds and transform into the two carbonyl groups.<sup>113</sup> If polymeric product contains ROMP unit in its backbone, the reaction of osmium tetroxide with periodic acid should cause a significant molecular weight drop. The GPC analysis before and after the oxidation reaction showed no difference in molecular weight. Hence, we firmly can rule out the ROMP possibility.

**Scheme 3.14:** ROMP of monomer **3**.





**Figure 3.18:** NMR spectra of (a) poly-romp-3 in CDCl<sub>3</sub> and (b) polymer sample from reaction 3 with CpZrCl<sub>3</sub> in CDCl<sub>3</sub>

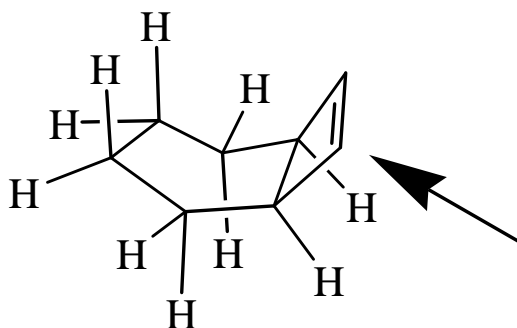
**(2) Thermal transformation of **3** to 1,3-cyclooctadiene followed by 1,2- or 1,4-  
enchainment polymerization.**

Since the transformation of 1,3-cyclooctadiene to **3** is mediated by heat, there is a slight chance of a reverse reaction. Although we did not detect any trace of 1,3-cyclooctadiene, we tried to polymerize 1,3-cyclooctadiene with same catalyst system. The reaction did not yield any polymer and we recovered only starting material. This hypothesis also was ruled out.

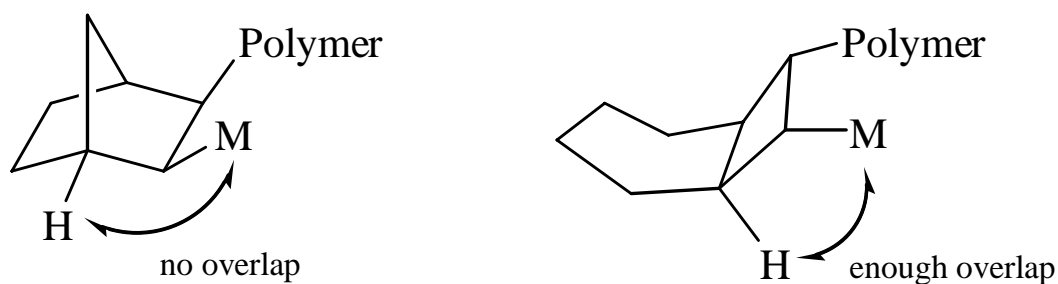
**(3)  $\beta$ -Hydride elimination**

$\beta$ -Hydride elimination is not a possible process in the case of norbornene, because it has limited orbital overlap and a resulting bridgehead double bond is prohibited by Bredt's rule. Now we ask the question, "how significant  $\beta$ -hydride elimination is in the case of our monomer **3**?".

The optimal conformation of monomer **3** is calculated at the Hartree-Fock level.<sup>114</sup> According to this calculation, the cyclohexane ring forms a boat conformation and whole molecule bends up like a bowl, Figure 3.19. It is assumed that catalyst center approaches from convex face of molecule to coordinate, similar to the case of norbornene. The resulting metal alkyl species could have enough overlap between the metal-carbon bond and the  $\beta$ -hydrogen bond, Figure 3.20.



**Figure 3.19:** Optimal conformation of monomer **3**.

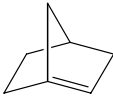




**Figure 3.20:** Schematic representation of metal- $\beta$ -hydrogen overlap.

Schleyer and his co-workers calculated ring strain of bridgehead olefins using empirical force field program and published a paper titled “Evaluation and Prediction of the Stability of Bridgehead Olefins”.<sup>100</sup> Olefinic strain (OS) is formulated by subtracting the total strain energy of the most stable conformer of the parent hydrocarbon from the total strain energy of the olefin, also in the most stable conformation. Unfortunately data for monomer **3** is not listed, however ring strain energies of the bridgehead olefin compounds from norbornene and monomer **4** are listed in their report, which is summarized in Table 3.4. In the course of this investigation, they reached the following empirical rules of bridgehead olefins, which is derived from OS.

Isolable bridgehead olefins    OS < 17 Kcal/mol  
 Observable bridgehead olefins    17 Kcal/mol < OS < 21 Kcal/mol  
 Unstable bridgehead olefins    OS > 21 Kcal/mol

**Table 3.4:** Strain energies of bridgehead olefins calculated by Maier *et al.*<sup>100</sup>

Bridgehead Olefin	Olefinic Strain (Kcal/mol)
	35
	17
	Not listed

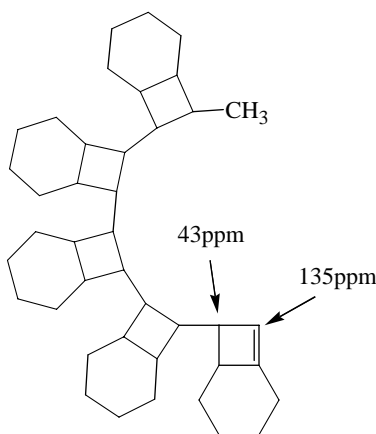
According to these criteria, norbornene is not able to  $\beta$ -hydride eliminate as it is generally accepted and monomer **4** is on the boundary.

There is no strain energy data for bridgehead compound from monomer **3**, however there is a report that bridgehead double bond compound is stable enough for isolation.<sup>115</sup> Existence of such bridgehead compound means that  $\beta$ -hydride elimination is a plausible explanation for the olefin structure found in the products, and also it explains the reason that no polymerization activity was shown with late transition metal catalysts.

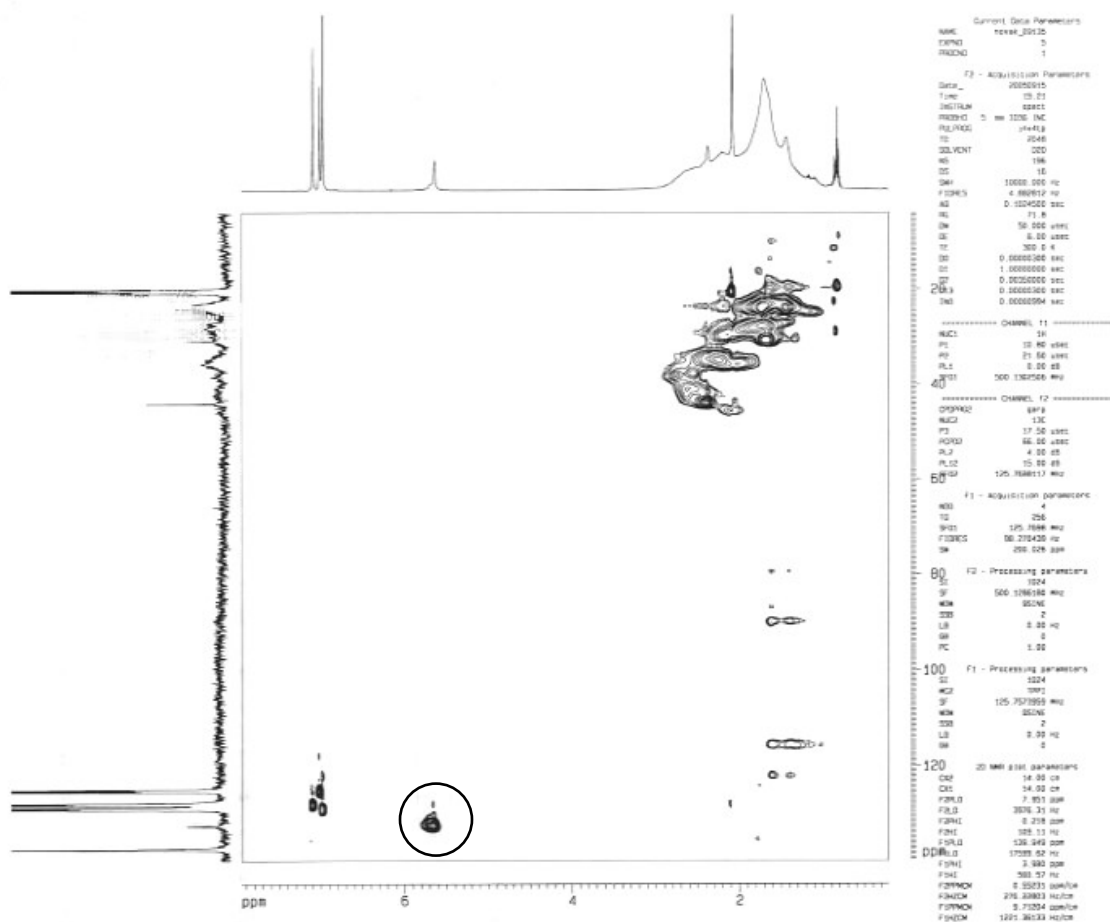
A drastic color change was observed at a very early stage in the polymerization attempt of monomer **3** with nickel acetylacetonate and tris(pentafluorophenyl)borane system (Table 3.3, run 1). This color change is not usually observed during norbornene polymerization. In addition, this same color change was also observed when monomer **3** was

added to a polymerization of norbornene with the same catalyst system. In nickel acetylacetonate with tris(pentafluorophenyl)borane catalyst system, the resulting nickel hydride species from  $\beta$ -hydride elimination is not capable of re-inserting the polymerization. The  $\beta$ -hydride elimination reaction literally terminates the polymerization (see Figure 3.14).<sup>86,90</sup>

To help confirm the bridgehead olefin structure at the terminal repeat unit, we employed 2D-NMR experiments.  $^1\text{H}$ - $^{13}\text{C}$  short range (one bond correlation) and long range (two bonds correlation) of polymeric sample from monomer **3** (Table 3.3, run 6), are shown in Figure 3.22 and Figure 3.23. The olefin proton peak clearly shows correlation with corresponding carbons on both the short range and long range spectra, which appear 132 ppm and 44 ppm, respectively. These two carbon peaks are well matched with predicted values shown in Figure 3.21.



**Figure 3.21:** Predicted  $^{13}\text{C}$  chemical shifts of **poly-3** with terminal olefin.

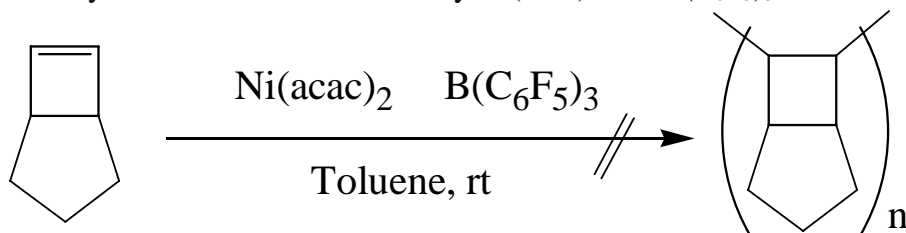


**Figure 3.22:** Short range  $^1\text{H}$ - $^{13}\text{C}$  correlation NMR spectrum of polymeric sample from monomer **3** with  $\text{CpZrCl}_3$  in toluene- $\text{d}_8$ .



Based on olefinic strain analysis, monomer **4** might have more potential to polymerize when catalyzed by late transition metals than monomer **3**, because of its moderately high strain energy. We attempted the polymerization of monomer **4** with nickel acetylacetonate and tris(pentafluorophenyl)borane, Scheme 3.15. Surprisingly, the reaction did not proceed. Although the reaction did not yield polymeric product, we observed an interesting phenomenon. There was no obvious color change during reaction; this observation is in clear contrast to the case of monomer **3**.

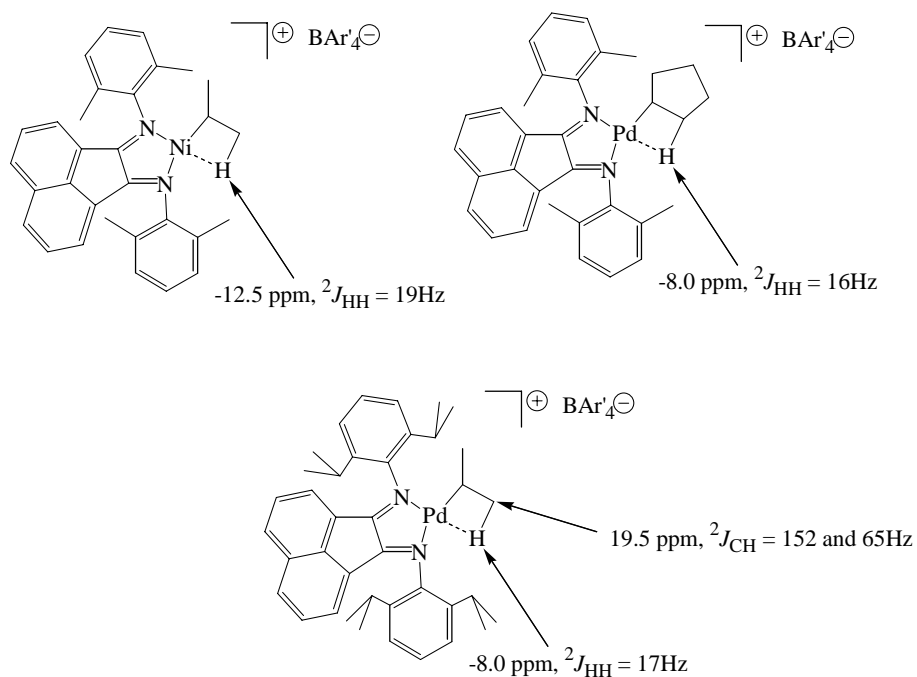
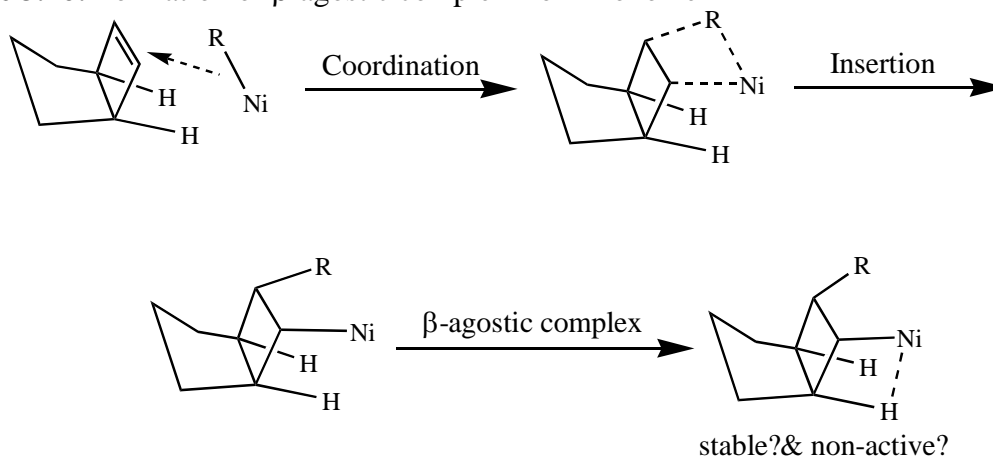
**Scheme 3.15:** Polymerization of monomer **4** by  $\text{Ni}(\text{acac})_2$  and  $\text{B}(\text{C}_6\text{F}_5)_3$



No color change indicates the active species may still be intact, which means no  $\beta$ -hydride elimination has taken place. The optimal conformation of monomer **4** by simulation also adopts a cup shape conformer as monomer **3** does. Nickel metal center and  $\beta$ -hydrogen would be in close proximity after an insertion; nevertheless no  $\beta$ -hydride elimination takes place. How does it happen? A plausible explanation is that  $\beta$ -agostic complex that is usually forms prior to  $\beta$ -hydride elimination is stable and prevent further coordination step, Scheme 3.16. It is reported that  $\beta$ -agostic complex of palladium or nickel is stable enough to observe

using magnetic resonance only at very low temperature, Figure 3.24.<sup>116-118</sup> We tried to observe the magnetic resonance of  $\beta$ -agostic complex of monomer **4**.

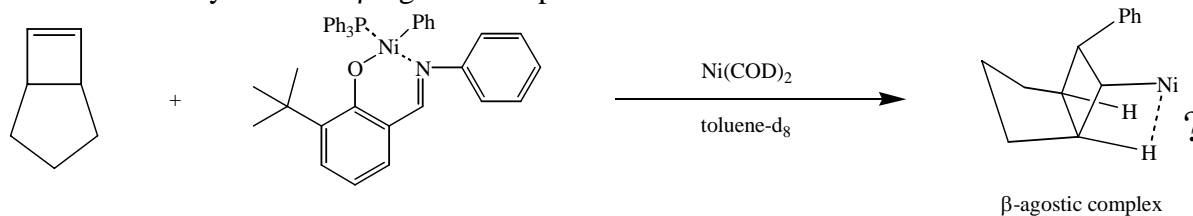
**Scheme 3.16:** Formation of  $\beta$ -agostic complex from monomer **4**



**Figure 3.24:** Chemical shift of  $\beta$ -agostic complex at  $-110 \sim -130$  °C in  $\text{CDCl}_2\text{F}$ .<sup>116-118</sup>

Since the nickel acetylacetonate and tris(pentafluorophenyl)borane catalyst system is not well-defined, we employed the well-defined Grubbs type neutral nickel catalyst system for the NMR experiment to look for agnostic interactions. In toluene- $d_8$  monomer **4** was allowed to react with a stoichiometric amount of Grubbs' nickel complex, activated by bis(cyclooctadiene) nickel in an NMR tube, Scheme 3.17. Because there is no geminal hydrogens, it is impossible to confirm the existence of a  $\beta$ -agostic complex by observing splitting of the signal. Hence, we conducted 2D-NMR,  $^1\text{H}$ - $^{13}\text{C}$  correlation (HMQC), with our sample. The reaction was slow and after 7 hours, an up field peak was observed at  $-2.2$  ppm, which has no correlation with other hydrogens and has correlation with carbon at 30 ppm. Although this peak appeared to be relatively weak, its chemical shift is reasonable for an agnostic interaction taking into account that we used neutral nickel species. Note the examples in Figure 3.24 are cationic. We believe this is evidence for the formation of a  $\beta$ -agostic complex.

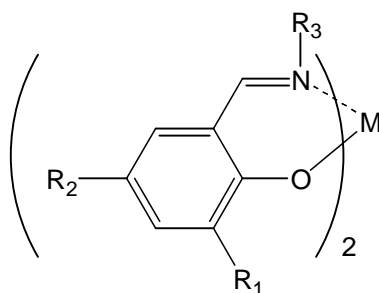
**Scheme 3.17:** Synthesis of  $\beta$ -agostic complex from monomer **4**.



Taken in total, the olefin structure in our product appears to be derived from  $\beta$ -hydride elimination, which we did not expect to proceed with monomer **3**. We feel  $\beta$ -hydride elimination is also responsible for the lack of polymerization reactivity with the late transition metal catalyst systems.

### 3.5.4 New Zirconium Catalyst

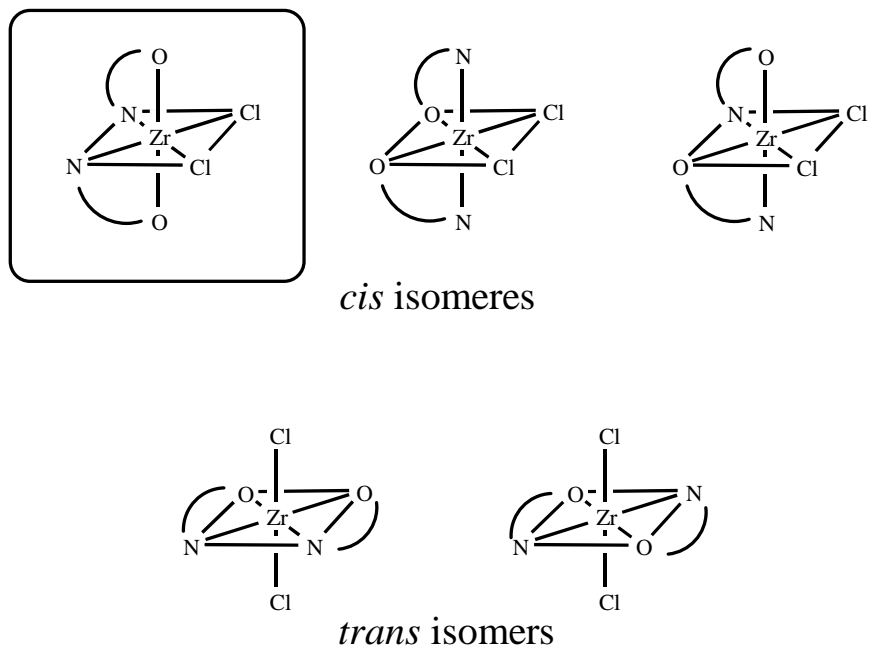
There is the family of zirconium catalysts, which is developed in Mitsui Chemical Company, see Chapter 3.1. (We refer this type catalyst in this paper as “Mitsui”.) The general structure of these complexes is shown below. There are many types of zirconium base coordination polymerization catalysts, and among those catalysts the Mitsui type catalyst is relatively easy to synthesize in few steps, and has a high polymerization activity and the capability to catalyze norbornene polymerization. Hence, we targeted the Mitsui catalyst.



This bis(phenoxy-imine) zirconium dichloride could have five possible isomeric structures, Figure 3.25. By DFT calculations one of *cis* isomers has lowest energy and it has been confirmed by X-ray crystallography.<sup>119</sup> It is important that two chloride atoms are situated in a *cis* fashion in order for the coordination-insertion chemistry to occur.

Steric hindrance around the metal center dominates catalytic performance and can be tuned by the bulkiness of substituents on phenyl group and/or imine nitrogen. In the case of ethylene polymerization, effects of substituent were studied well; more bulky substituent on

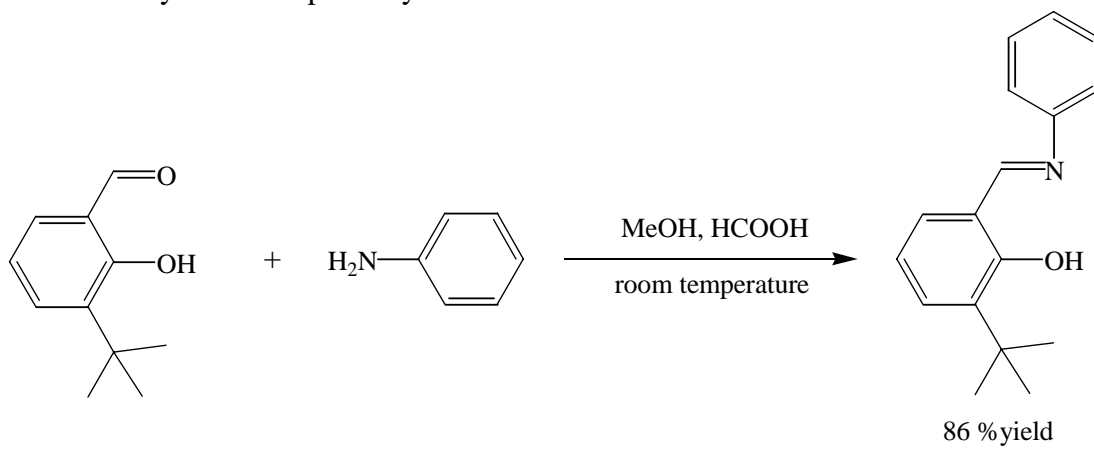
the ortho position ( $R_1$ ) mainly enhances the activity and more bulky substituents on the imine nitrogen ( $R_3$ ) mainly enhances the molecular weight. Those changes on different substituents are explained by both effective separation of the cation-anion pair, which gives monomers more space to coordinate, and by destabilizing the transition state for  $\beta$ -hydride elimination.



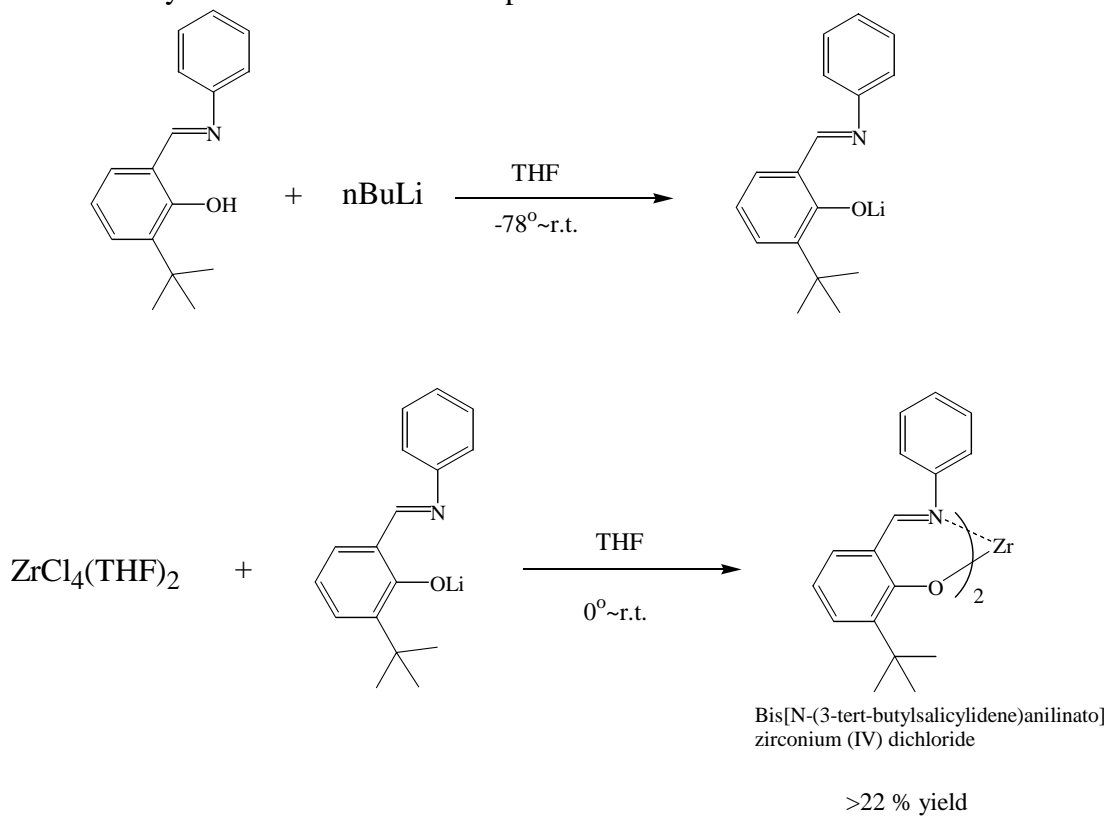
**Figure 3.25:** Five possible isomers for Mitsui catalyst

The phenoxy-imine ligand is synthesized through imine formation of the corresponding aldehyde/ketone and an amine with generally high yields.<sup>119</sup> Since our monomer is more bulky than ethylene, we chose a relatively less sterically congested ligand, Scheme 3.18. Complex formation was achieved by using 2 equivalent of the lithium salt of the ligand with zirconium tetrachloride tetrahydrofuran complex, Scheme 3.19.

**Scheme 3.18:** Synthesis of phenoxyimine



**Scheme 3.19:** Synthesis of zirconium complex



A polymerization attempt of monomer **3** in toluene with Mitsui zirconium complex activated by 3,400 equivalent of methyl aluminoxane (MAO) afforded a polymeric product with moderate yield, Table 3.5 run 1. The polymeric product precipitated as the reaction progressed in toluene, which implied poor solubility in this solvent. In fact, the solubility was found to be poor in toluene and chloroform. However, halogenated benzene derivatives, such as 1,2-dichlorobenzene, dissolve this product at room temperature.

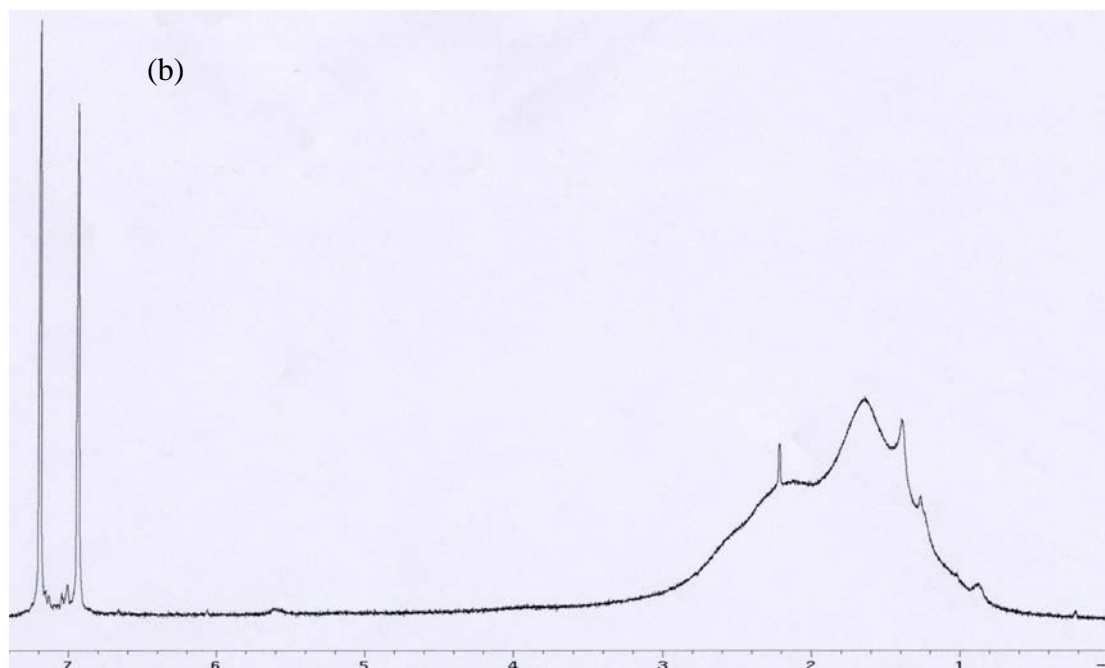
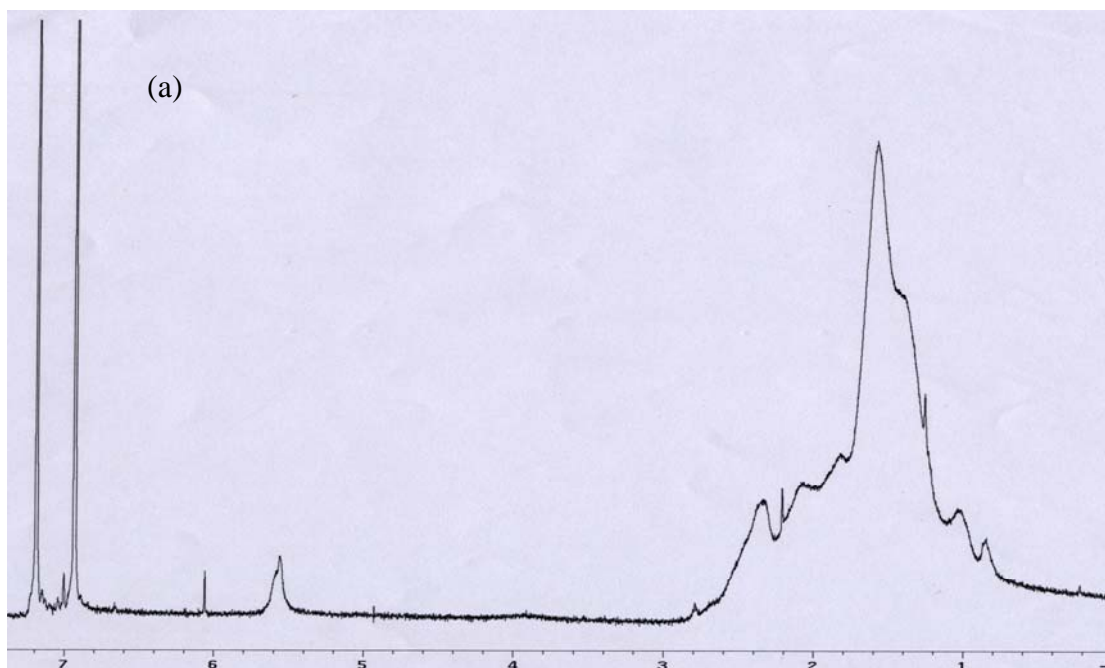
**Table 3.5:** Monomer **3** polymerization with Mitsui Zr with MAO.

Run	Co-monomer	Zr cat. ( $\mu$ mol)	MAO (mmol)	solvent	Yield (g)
1	-	10	34.0	Toluene (20 mL)	0.64
2	-	10	34.0	Toluene/o-DCB=1/1 (40 mL)	0.71
3	-	10	34.0	Toluene (40 mL)	0.46
4	Ethylene (50 mL/min)	10	34.0	Toluene (25 mL)	1.62 (972kg/molZr·h)

\* 1.0 g (0.94mol) of monomer **3** was used. Room temperature.

The  $^1\text{H}$ -NMR spectra of the polymer obtained using the cyclopentadienyl zirconium trichloride catalyst, Table 3.3 run 6 and Mitsui zirconium, Table 3.5 run 1 are shown in Figure 3.26. A diminished olefin peak is clearly seen in the material obtained using the Mitsui catalyst.

Because we assumed that a poor solubility of the product could cause lowering of the yield, we then tried mixed solvent and highly diluted solution to improve product yield; however we could not find any improvement, Table 3.5 run 2 and 3.

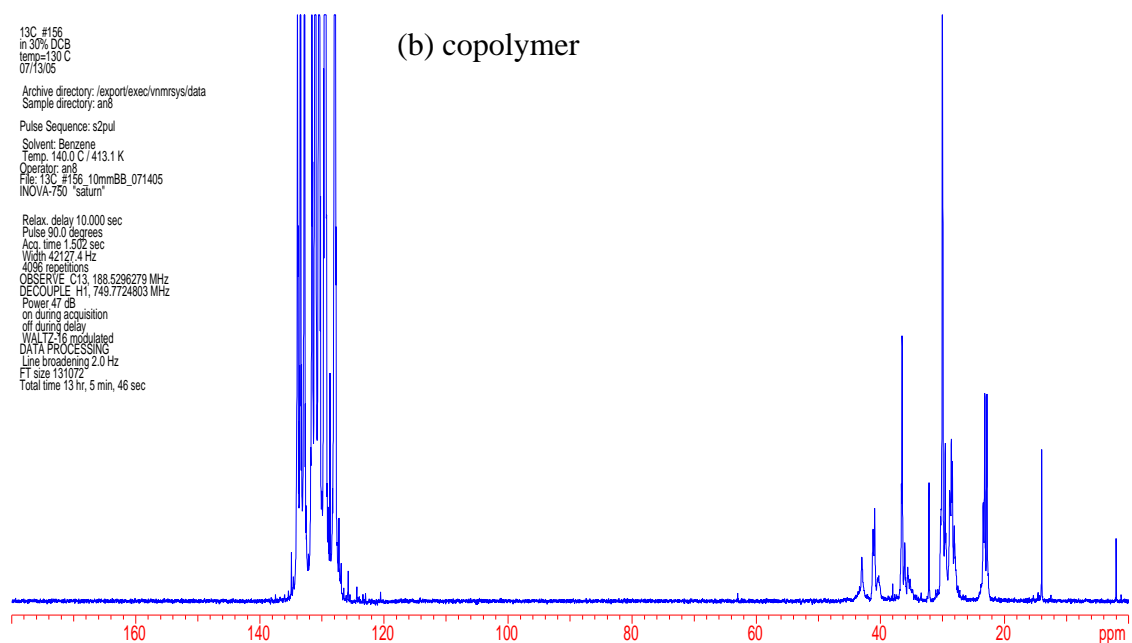
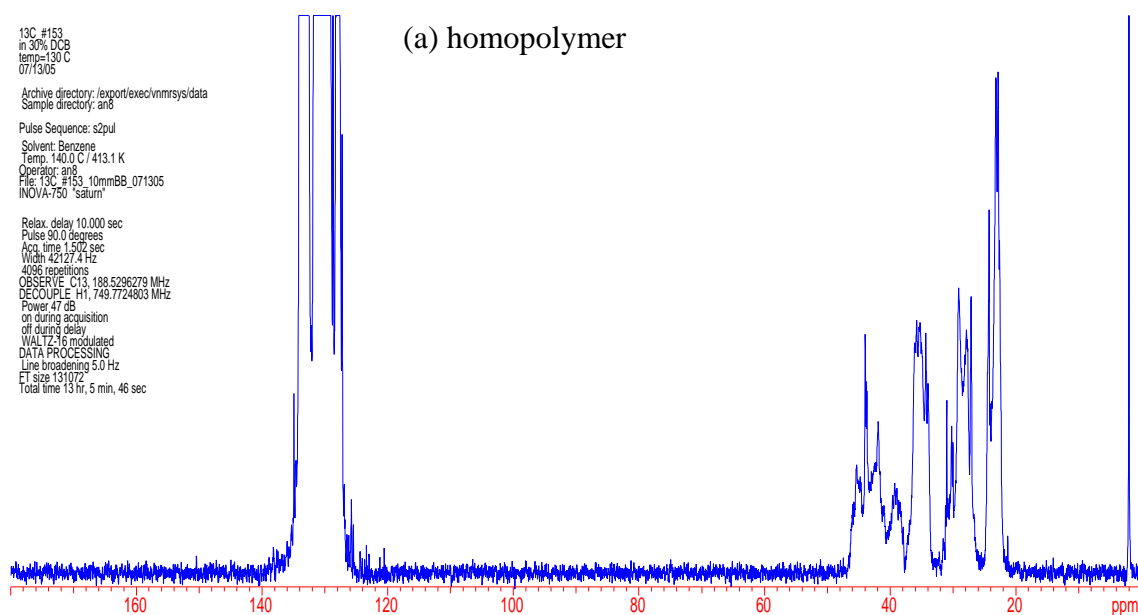


**Figure 3.26:**  $^1\text{H}$ -NMR spectra of polymeric product from monomer **3** (a) catalyzed by  $\text{CpZrCl}_3$  and (b) catalyzed by Mitsui Zr, in  $o\text{-DCB-d}_4$  at room temperature.

Bulky monomer do not always compete well with ethylene, but it was also discovered that monomer **3** will copolymerize with ethylene. The copolymerization of monomer **3** with ethylene was successful, table 3.5 run 4. Ethylene-**3**-copolymer is not soluble at room temperature, so we performed high temperature  $^{13}\text{C}$ -NMR of the homopolymer and copolymer, Figure 3.27. The differences between the two spectra clearly indicate formation of a random copolymer, and does not indicate a mixture of two homopolymers or block copolymer. Monomer incorporation ratio is calculated ethylene/**3** = 5/1 based on quantitative  $^{13}\text{C}$ -NMR.

We also performed high temperature GPC analysis of these two samples, Table 3.6 and Figure 3.28. It is revealed that both polymers have quite low molecular weight and very broad polydispersity that almost look bimodal.

These data suggest that a lot of chain transfer reaction occurred during polymerization, and furthermore the chain transfer reaction does not seem to include  $\beta$ -hydride elimination based on very little olefin signals.

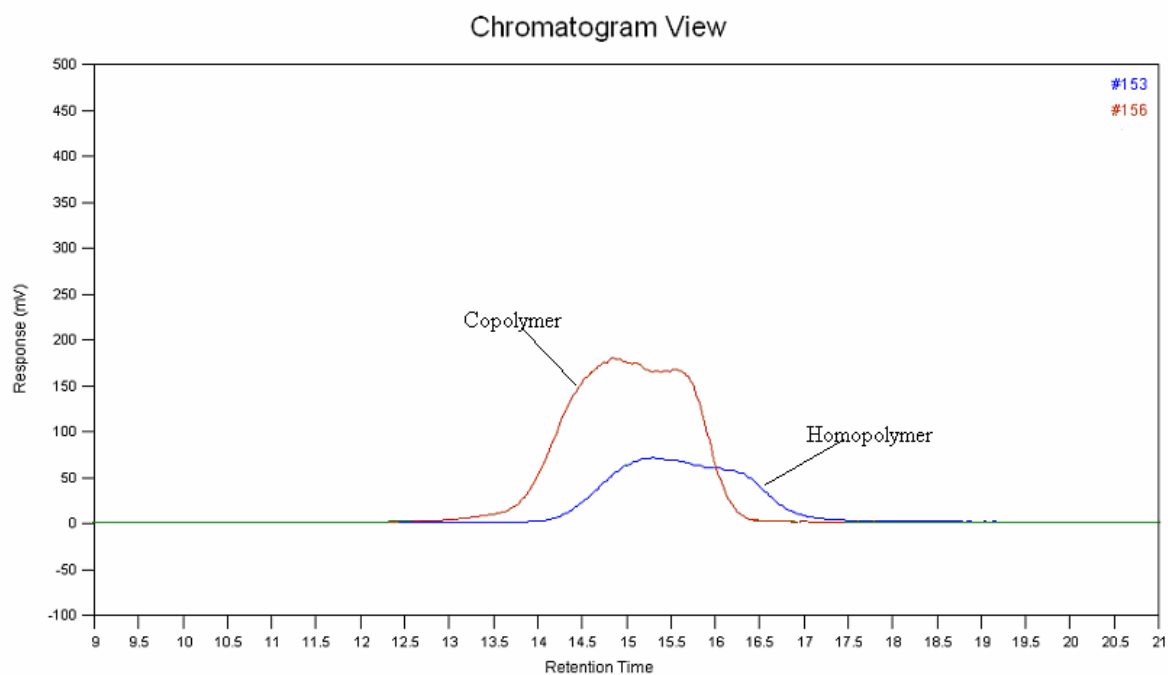


**Figure 3.27:** <sup>13</sup>C-NMR spectra of (a) monomer **3** homopolymer and (b) ethylene monomer **3** copolymer at 130°C in o-DCB-d<sub>4</sub>.

**Table 3.6:** Molecular weight of selected samples.

Run	Co-monomer	solvent	Yield (g)	Mw	Mn	Mw/Mn
1	-	Toluene (1g monomer in 20 mL)	0.64	3,300	1,100	3.0
2	-	Toluene/o-DCB=1/1 (1g monomer in 40 mL)	0.71	-	-	-
3	-	Toluene (1g monomer in 40 mL)	0.46	-	-	-
4	Ethylene	Toluene (1g monomer in 25 mL)	1.62g yield (972kg/molZr-h)	8,200	3,600	2.3

\* 1.0 g (0.94mol) of monomer **3** was used. Room temperature. Molecular weight is relative to polystyrene.

**Figure 3.28:** GPC comparison of homopolymer and copolymer.

### 3.5.5 Chain Transfer Reaction (co-catalyst study)

The active species in group IV metallocene/non-metallocene catalyst systems have been determined to be coordinatively unsaturated cationic species, which can be generated from dialkyl complexes combined with an activator such as tris(pentafluorophenyl)borane, or from halogenated complexes combined with an activator such as methylaluminumoxane (MAO). Several groups have reported that the activators can influence not only the productivity of polymerization but also the structure of the resulting polymers, such as molecular weight,<sup>120-123</sup> stereoregularity<sup>123-128</sup> or regioregularity.<sup>128,129</sup>

Common features of olefin coordination polymerization catalyst systems are  $\beta$ -hydride elimination and chain transfer reactions that terminate the growth of a polymer chain and result in the initiation of a new polymer chain by the catalyst. This produces a number of low molecular weight polymer chains. For example, in metallocene catalysts, consecutive olefin insertion into the metal-carbon bond of the polymer chain proceeds until  $\beta$ -hydride elimination occurs. When alkyl aluminum compounds are employed as activators, an additional termination route is chain transfer to the aluminum center. Several strategies have been devised to decrease the rate of chain termination relative to that of propagation such that longer polymer chains can be formed. The simplest solution in many cases is simply lowering the polymerization temperature. Since the  $\beta$ -hydride elimination process is unimolecular while propagation is bimolecular, a lowering in temperature more adversely affects the elimination processes relative to insertion. Since precipitation of polymers from solution during polymerization at low temperatures can hinder the controlled nature of polymerization, it is generally advantageous to perform reactions at ambient temperature.

Therefore, a second strategy is to eliminate the use of alkyl aluminum activator that gives the potential for chain-transfer reactions. In this regard, the development of weakly coordinating anions has made significant advances in olefin polymerization.

In the case of halogenated catalyst precursor complexes, the use of alkylating agent, such as alkyl aluminum or MAO, is necessary. It is known that MAO solutions contain “free” trialkylaluminum, which acts as a chain transfer agent and/or lowers the productivity. Since the resulting polymer chain from chain transfer to aluminum does not contain olefin structure at terminal, we assumed that this residual trialkylaluminum caused chain transfer reactions and gave such a low molecular weight polymer in our monomer system.

MAO is well known as an activator of single site catalysts of olefin polymerization. Despite a significant amount of research, the details of its structure have yet to be determined. The proposed structure of MAO is a mixture of linear or cyclic chains which contain 3- and 4-coordinated aluminum species.

Although the structure of MAO still remains unknown, techniques have been found to improve the productivity with MAO. Shiono and co-workers studied the effect of reduction or addition of “free” trialkylaluminium or arylborane to MAO for propylene polymerization.<sup>122</sup> The catalyst used in their research was  $[t\text{-BuNSiMe}_2(\text{C}_5\text{Me}_4)]\text{TiMe}_2$ . After treatment for 4 hours under high-vacuum and following wash with hexane, trimethylaluminum effectively was removed from standard MAO. They found this “dried” MAO more active than standard MAO and polymer produced has a higher molecular weight. They also investigated ability of chain transfer reactions by various types of alkylaluminum complexes. They examined the effects of methyl-, ethyl-, iso-butyl-, and octyl-aluminum

added to polymerizations activated by “dried” MAO. Based on the molecular weight and number of polymer chains, they concluded the chain transfer ability to follow this order:  $\text{Et}_3\text{Al} > \text{isoBu}_3\text{Al} \gg \text{Oct}_3\text{Al} \approx \text{Me}_3\text{Al}$ .

MAO producer Akzo Nobel developed so-called modified MAO whose formula is  $[(\text{CH}_3)_{0.7}(\text{isoCH}_2\text{H}_9)_{0.3}\text{AlO}]$ . Modified MAO is known to have higher activity and stability than standard MAO. Researchers in Sumitomo Chemical R&D center reported further modification of modified MAO to improve activity. They reported that an addition of water and pentafluorophenol greatly enhanced molecular weight by three orders of magnitude when the catalyst precursor thiobis(phenoxy)-titanium dichloride was activated by modified MAO in a 1-butene polymerization.<sup>130</sup> They did not speculate on the origin of this enhancement, however, after modification with water and pentafluorophenol they confirmed a change in the coordination number of aluminum, six coordination to five coordination, by means of  $^{27}\text{Al}$ -NMR. They then tentatively concluded that the different coordination number species may play an important role in the improved activation.

Fujita and his co-workers in Mitsui Chemical also reported variation of the activators for their own catalysts.<sup>131</sup> A combination of triisobutylaluminum and triphenylmethyl tetrakis(pentafluorophenyl)borate was used for activation on ethylene polymerization. Although this system showed less productivity than MAO system, resulting polymer has ten times higher molecular weight than from MAO system.

An additional amount of MAO added is critical to activate catalyst precursor and it influences the productivity of the polymerization. In general, the amount of MAO required to efficiently activate a system probably ranges from 250 to 3,000 equivalent to precursor

depending on catalyst. A simple way to reduce the amount of trimethylaluminum to eliminate unwanted chain transfer is to lower the amount of MAO used to activate.

Taking all these possible solution under consideration, we conducted activator modification experiments in attempt to produce high molecular weight **poly-3**, Table 3.7. All catalyst and activator combinations produced polymers. All the materials obtained were not soluble in 1,2-dichlorobenzene at room temperature, so high temperature GPC was performed.

These results clearly show that reducing the amount of MAO down to 500 equivalent produced high molecular weight **poly-3** with excellent productivity, run 2. Polydispersity lower than 2.0 indicate single active species. Water and pentafluorophenyl modified MAO showed little improve on yield but molecular weight. “Dried” MAO also produced much higher molecular weight with good productivity, run 3. Finally, the modified MAO also showed high productivity.

**Table 3.7:** Results of activator modification to polymerize monomer **3**.

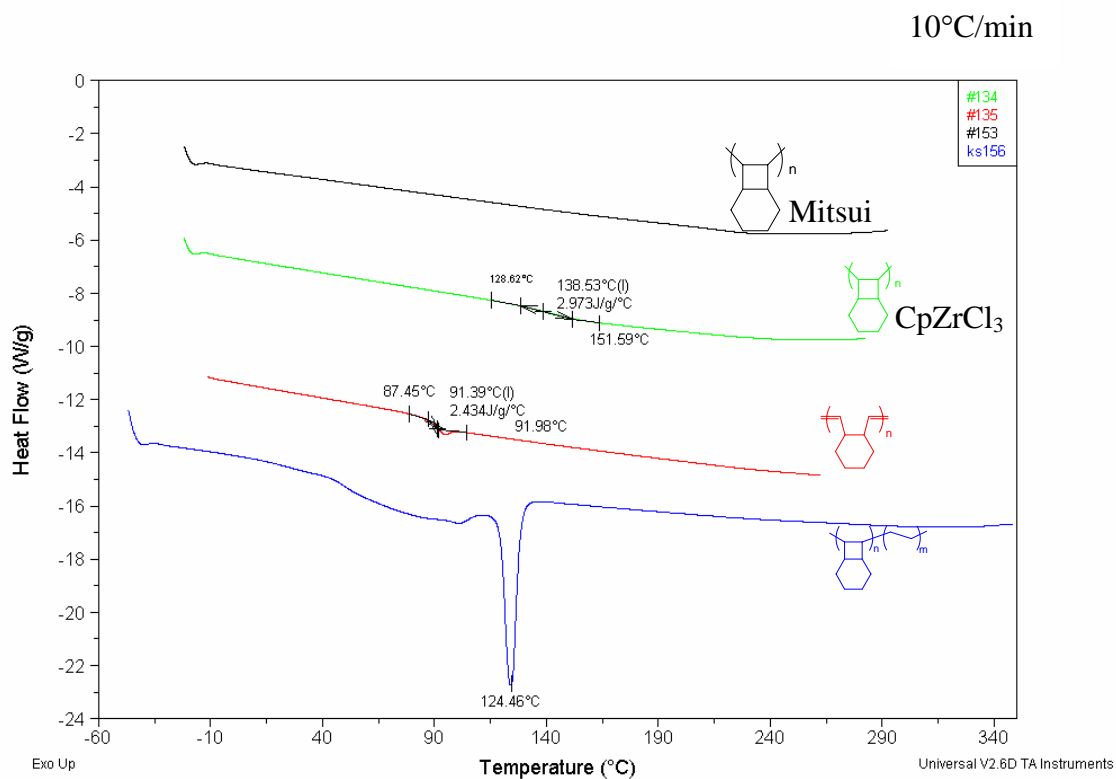
Run	co-catalyst	Yield (g)	Mw	Mn	Mw/Mn
1	MAO 3,400 eq	0.64	3,300	1,100	3.0
2	MAO 500 eq	0.97	219,000	141,000	1.6
3	“dried” MAO 500 eq	0.83	164,000	99,000	1.7
4	MAO 500 eq, H <sub>2</sub> O 100 eq, C <sub>6</sub> F <sub>5</sub> OH 100 eq	0.90	7,400	2,100	3.5
5	iso-Bu <sub>3</sub> Al 40 eq, Ph <sub>3</sub> C(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> 2 eq	0.14	2,400	700	3.4
6	Oct <sub>3</sub> Al 20 eq, B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> 10 eq	trace	-	-	-
7	iso-Bu <sub>3</sub> Al 150 eq, MAO 350 eq, H <sub>2</sub> O 150 eq	0.86	245,000	155,000	1.6

\* 1.0 g (0.94mol) of monomer **3** was used. Room temperature. 10.0  $\mu$ mol of Zr cat was used. Molecular weight is relative to polystyrene.

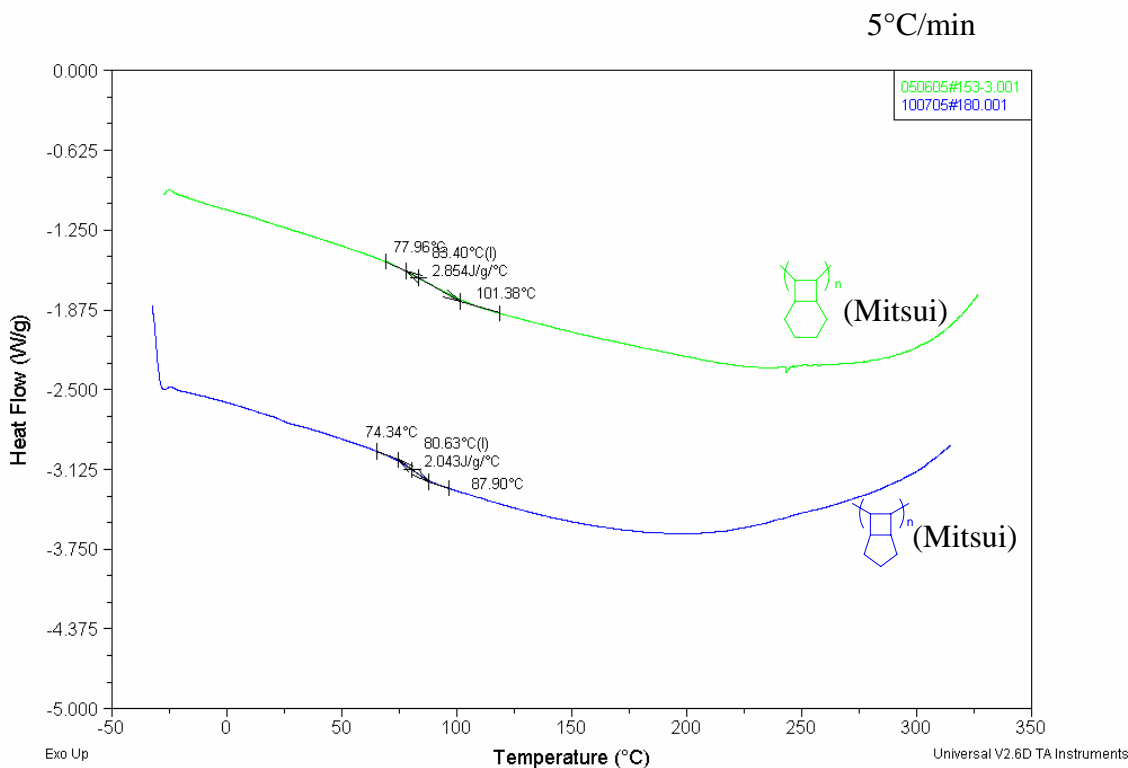
### 3.6 Characterization of The Polymers

#### 3.6.1 Thermal Analysis

Thermogravimetric analysis revealed that both **poly-3** and **poly-4** have thermally stabilities close to 400°C even with very low molecular weights. Differential scanning calorimetric analysis of samples with very low molecular weights are shown in Figure 3.29. **Poly-3** sample from CpZrCl<sub>3</sub> system has glass transition temperature around 140°C whereas **poly-3** sample from Mitsui catalyst has no phase transition. However, when rate of temperature was changed to 5 °C from 10 °C, detectable phase transition appeared on both **poly-3** and **poly-4**, Figure 3.30.



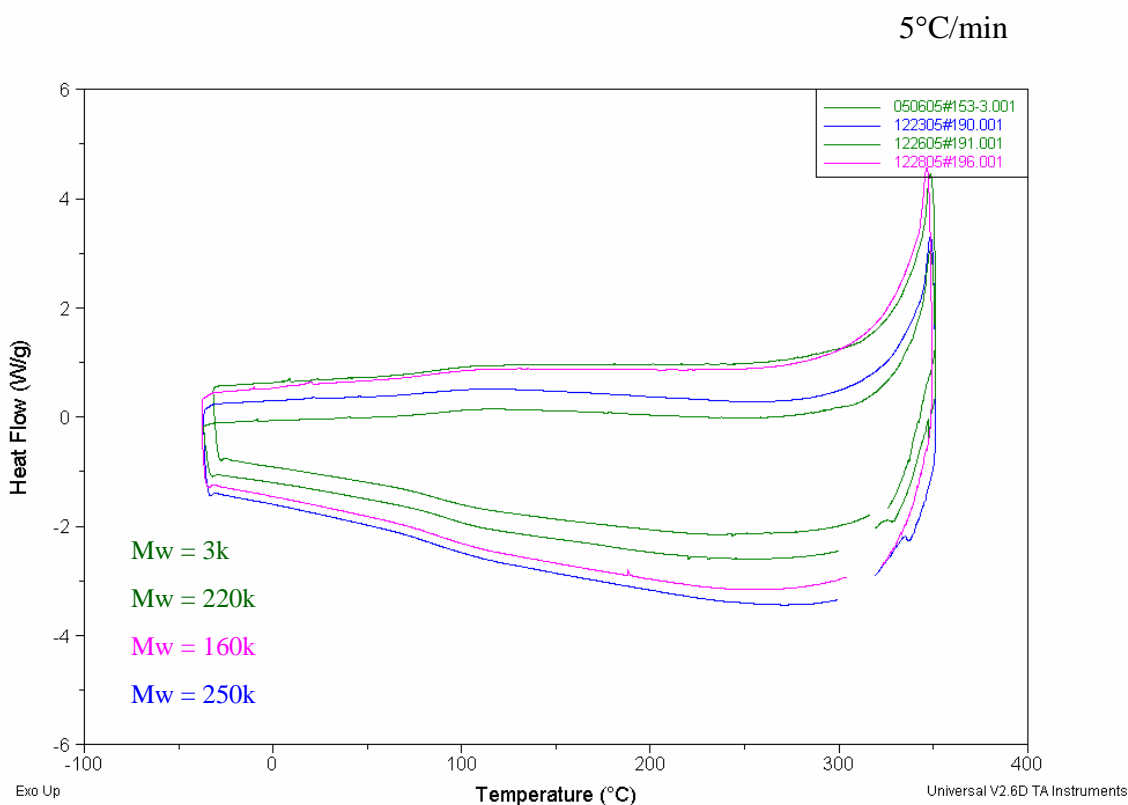
**Figure 3.29:** DSC analysis of selected samples and low molecular weight **poly-3** (Mw = 3,300).



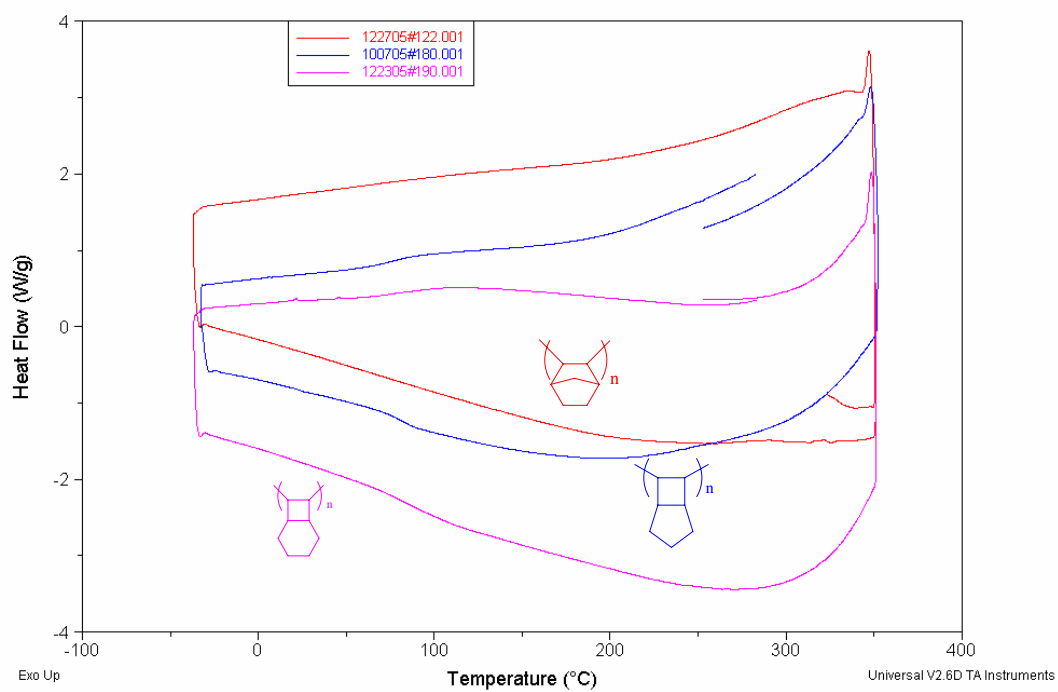
**Figure 3.30:** DSC analysis of low molecular weight **poly-3** ( $M_w = 3,300$ ) and **poly-4** (unknown  $M_w$  due to insolubility) at slower rate of temperature ( $5^\circ\text{C}/\text{min}$ ).

Both polymers have almost same glass transition temperature at around  $80^\circ\text{C}$ . Since we expected our polymers to possess similar thermal behavior as polynorbornenes do, this was quite a surprising result to us. However, this low  $T_g$  might due to low molecular weight. After activator studies, we obtained very high molecular weight samples of **poly-3**. DSC analysis of high molecular weight sample along with low molecular weight sample is shown in Figure 3.31. All four samples measured show  $T_g$ 's at same temperature no matter how high the molecular weight is.

Glass transition temperature depends on the microstructure of polymer, the rigidity of polymer main chain, steric bulk of side chain, and stereoregularity. High glass transition temperatures of polynorbornene,  $>340^{\circ}\text{C}$ , is understood to arise from its tightly connected bulky repeat unit and relatively regular microstructure, which results in tightly packed polymer chains (low free volume). The low glass transition temperature of **poly-3** could be due in part to a less tightly packed structure of polymer (higher free volume). The comparison of DSC curves of three polymers is shown in Figure 3.32.



**Figure 3.31:** DSC analysis comparison of various molecular weight samples of **poly-3**.



**Figure 3.32:** The comparison of DSC curves of three polymers, **poly-3**, **poly-4**, and polynorbornene.

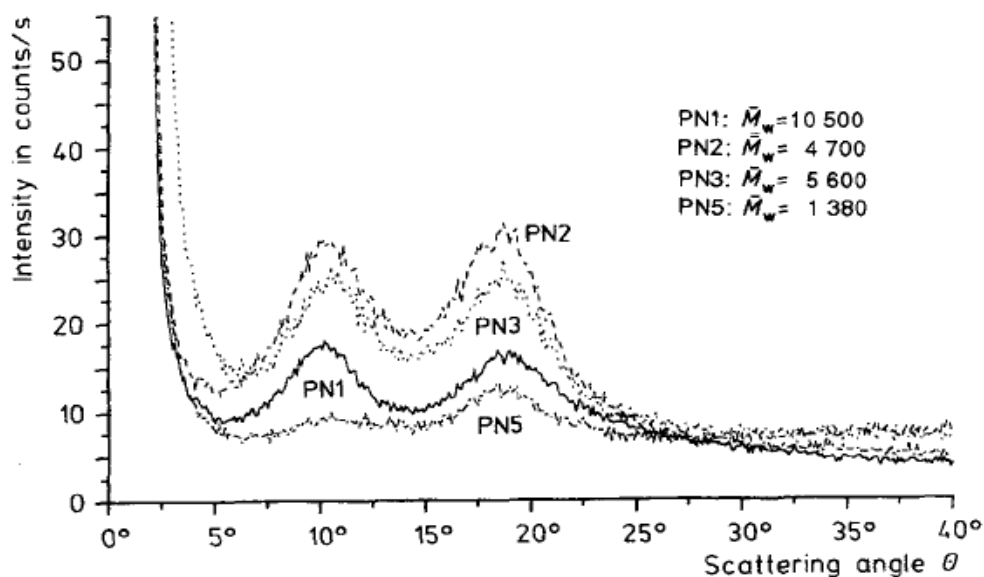
### 3.6.2 X-ray Powder Diffraction Analysis

It is known that polynorbornene is generally amorphous, but it is also known to display short-range order and high packing density.<sup>86,132-137</sup> This short-range order can be altered by conditions of polymerization or the type of catalyst used. The different degree of short-range order influences the solubility. Norbornene polymerized by palladium catalysts forms a polymer not soluble into any type of solvent even at high temperature, whereas nickel catalyzed polynorbornene is typically soluble in halobenzenes at high temperature.<sup>79,137</sup>

Heitz and his co-workers have done the research on the polynorbornene packing in the amorphous state.<sup>133</sup> In order to get a quantitative measure of the packing efficiency within the amorphous state, they compared the predicted Van der Waals volume, hard-core volume of the repeating unit, with the actual volume of the amorphous state. The ratio of the two values amounts came out to 1.43, which, according to them, is exceptionally high packing ratio when consider following numbers. Glassy polymers are in general characterized by an average ratio of 1.60, whereas crystalline polymers fall in an average ratio of 1.435. The obvious conclusion to be drawn is that the packing of the polynorbornene is very efficient, approaching the characteristic of a crystalline state. The high packing density may help to suppress motions within the glassy state. An insight into the actual short-range order is obtained from calculations on the amorphous cells. Researchers also used calculated data of cell dimensions by means of molecular dynamics simulations using the force field. The result is expressed by the radial distribution function, which is defined as the distribution of internuclear distances. The radical distribution function is characterized by the occurrence of

two maxima in the range of distances of about 6 and 10 Å. They also obtained these characteristic dimensions from the analysis of the wide-angle X-ray diffraction (WAXD) of polynorbornene sample powder, Figure 3.33. The wide-angle X-ray powder diffraction diagram reveals the presence of two broad halos in the wide-angle regime, which can be attributed to a short-range order. The distances derived from these halos using equation 7.<sup>138</sup> Bragg reflections characteristic of crystalline regions are not present. They concluded that this short-range order is derived from intrachain nature based on the amorphous cell calculations.

$$r \cong \frac{5}{4} \cdot \frac{\lambda}{2 \sin \theta} \quad (7)$$

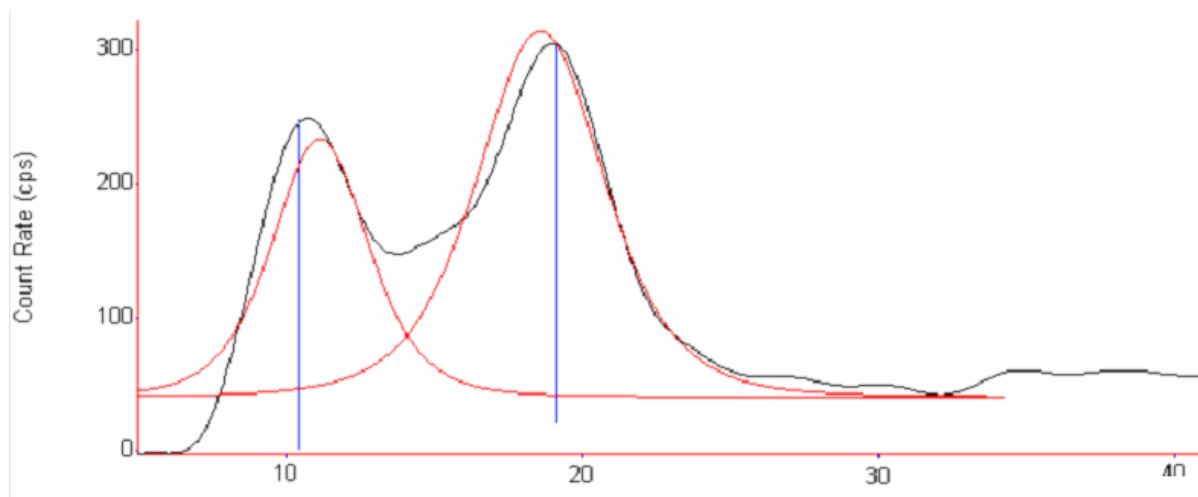


**Figure 3.33:** WAXD diagram of polynorbornene. (Reproduction from *Macromol. Chem. Phys.* **1996** 197 3435)

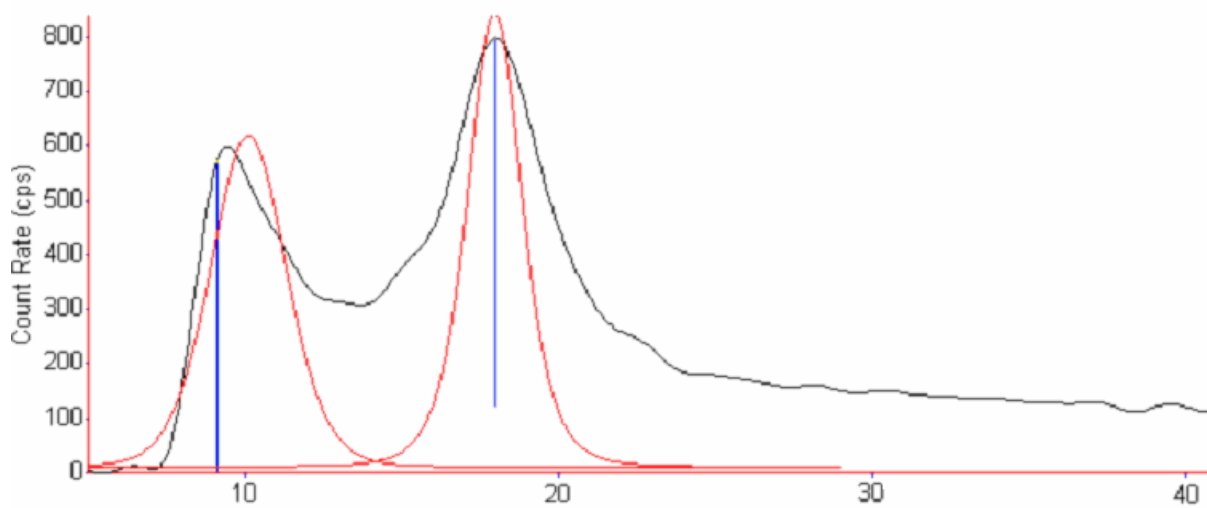
To evaluate the short-range order of **poly-3** and **poly-4**, WAXD analysis of three samples, polynorbornene, **poly-3**, and **poly-4** was carried out, Figure 3.34, 3.35, and 3.36. From X-ray diffraction pattern, short-range order distance was calculated, Table 3.8.

**Table 3.8:** The short-order distance derived from halos using Eq. (7).

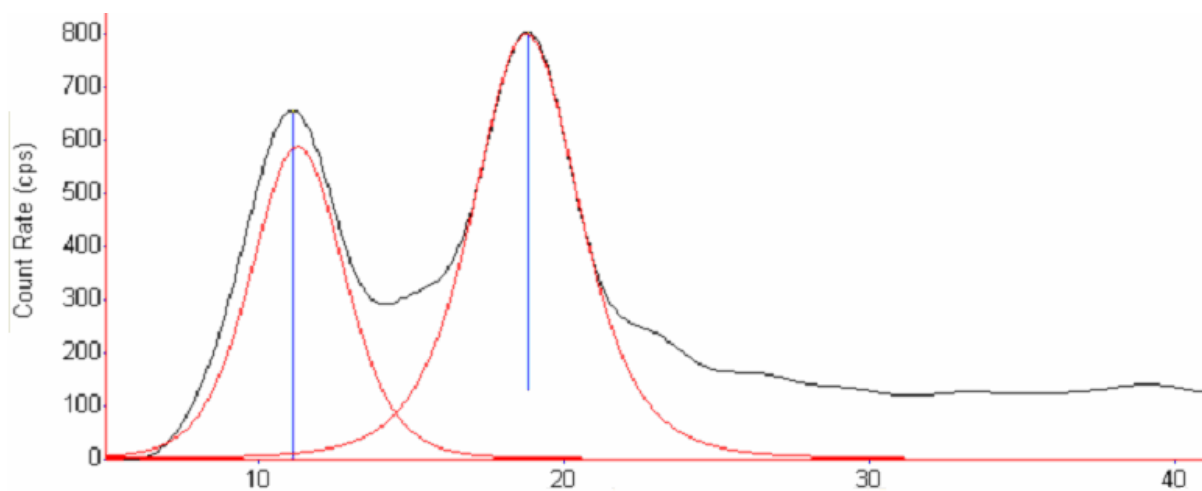
Polymer sample	Short-range order distance (Å)
<b>Polynorbornene</b>	5.96
	9.93
<b>Poly-3</b>	6.18
	10.93
<b>Poly-4</b>	5.91
	9.81



**Figure 3.34:** X-ray powder diffraction diagram of polynorbornene catalyzed by Ni(acac)<sub>2</sub>.



**Figure 3.35:** X-ray powder diffraction diagram of **poly-3** ( $M_w = 220,000$ ).



**Figure 3.36:** X-ray powder diffraction diagram of **poly-4** ( $M_w$  unknown, insoluble).

We obtained the same short-range order distances for polynorbornene as the values reported by Heitz. The WAXD diagram clearly showed that **poly-3** and **poly-4** also have short-range order in their polymer structures. Glass transition temperatures of **poly-3** and **poly-4** are much lower than polynorbornene, which is assumed because of less ordered or packed polymer chain structure. Based on the observed larger short-range order distances for **poly-3**, this loose packing may account for the lower Tg. However **poly-4** has almost same or shorter distances as does polynorbornene, so this packing argument cannot hold in this case.

At the glass transition temperature the molecules that are effectively frozen in position in the polymer glass become free to rotate and translate. The incorporation of units which impede rotation and stiffen the chain cause an increase in Tg.<sup>139</sup> Large and bulky side groups tend to cause greatest stiffening, however, if the side group is flexible the effect is not so marked. For example, polyethylene which has flexible chains show low Tg, -130°C ~ 0°C. When isobutyl group introduced to polyethylene Tg goes up to 50°C. On the other hand, the introduction of the ethyl group causes much less of an increase in Tg (-40°C), than the introduction of isobutyl group.

This side chain flexibility might explain such a low glass transition temperature of **poly-3** and **poly-4** compared to polynorbornene. Both **poly-3** and **poly-4** have relatively flexible side group than polynorbornene does. And this cyclohexyl side group may have enough flexibility to influence the Tg of polymer.

### 3.7 Conclusion

The coordination-insertion polymerization of bicyclo[4.2.0]oct-7-ene (**3**) and bicyclo[3.2.0]hept-6-ene (**4**) were reported. This is the first report that cyclobutene derivatives can be polymerized without side reactions such as pericyclic ring opening reactions or ring opening metathesis polymerization to afford high molecular weight addition polymers.

The late transition metal catalyst systems did not show any polymerization activity toward monomer **3**, which was against our expectation. Whereas cyclopentadienyl zirconium trichloride activated methylalminoxane shows moderate activity and resulting polymer contains a lot of olefin signals in its NMR spectra. The origin of olefin was confirmed as resulting from  $\beta$ -hydride elimination by means of 2D-NMR experiments.

Phenoxy-Imine type zirconium complex, bis[*N*-(3-*tert*-butylsalicylidene)anilinato] zirconium(IV) dichloride, which has been developed by Mitsui Chemical, shows excellent activity toward monomer **3** and **4** polymerizations when it is activated by methylalminoxane. This catalyst system also catalyzed ethylene-monomer **3** copolymerization. Low molecular weight polymer was obtained at early stage of our research, which was then resolved after we performed a number of activator studies. A reduced amount of methylalminoxane affords quite high molecular weight **poly-3**.

The trends in activity of monomer **3** towards early and late transition metal catalyst systems is opposite to that of norbornene.<sup>79</sup> Monomer **3** can be polymerized by early transition metal system but not by late transition metal systems.

Glass transition temperature ( $T_g$ ) of **poly-3** and **poly-4** are below 100°C, which is much lower than we expected based on similarity of repeat unit with polynorbornene that possess  $T_g$  at 340°C. Wide-angle X-ray powder diffraction was performed on **poly-3** and **poly-4**. It is revealed that the short-range order distances are close to polynorbornene, which requires another explanation for the low  $T_g$ . We now presume that side chain flexibility might play an important role.

### 3.8 Experimental Section

#### 3.8.1 General Procedures and Characterization

1,5-Cyclooctadiene, potassium tert-butoxide, acetophenone, 1,3-cycloheptadiene, 1,2-bis(phenylphosphino)-ethane, 3-*tert*butylsalicylaldehyde, aniline, glyoxal, 2,6-diisopropylaniline, 2,6-diacetylpyridine, *n*-butyllithium, methylalminoxane, *ti*isobutylalminum and were purchased from Aldrich Chemical Inc. and used as received. Pentafluorophenol was purchased from Tokyo Kasei Ltd. Nickel(II) chloride hexahydrate, (COD)PdCl<sub>2</sub>, iron(II) chloride tetrahydrate, zirconium(IV) chloride tetrahydroframate, nickel(II) acetylacetonato, bis(cyclooctadiene) nickel and zirconium monocyclopentadiene trichloride were purchased from Strem Chemicals Inc. and used as received except for nickel(II) acetylacetonato, which is recrystallized from benzene solution. Tris(pentafluorophenyl) borane and triphenylmethyl tetrakis(pentafluorophenyl) borate were provided from Albemarle Corp. as free sample. Water was purified through reverse osmosis filter.

Toluene, heaxane, benzene, dichloromethane, and ditheylether were purchased from Aldrich Chemical Inc. as anhydrous grade and used passing through Mbraun dry solvent system. Other solvents were purchased from Aldrich Chemical Inc. or Fisher Scientific with or without standard purification as needed. In the case of handling the air/moisture sensitive materials, Mbraun Unilab Dry-Box system was used as needed.

<sup>1</sup>H-NMR spectra were obtained using a Varian Mercury 400 (400 MHz), Varian Mercury 300 (300 MHz) spectrometers, Bruker AVANCE 500 (500 MHz), or Varian Inova 750 (750 MHz) as specified. Chemical shifts are reported in  $\delta$  (ppm) and are referenced to

selected residual proton peaks for the solvents or to internal standard. Significant  $^1\text{H}$  NMR data are tabulated in the following order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br: broad), coupling constant in Hertz, number of protons.  $^{13}\text{C}\{^1\text{H}\}$  proton decoupled NMR were measured at 100 MHz on a Varian Mercury 400. Chemical shifts are reported in  $\delta$  (ppm) and are referenced to peaks of solvents as follows or to internal standard.

The gel permeation chromatography was performed using 2 PL gel Mixed B columns and evaporative light scattering detector (ELSD) in trichlorobenzene at 160 °C. All samples were prepared at approximate concentrations of 2 mg/mL in HPLC grade 1,2,4-Trichlorobenzene (TCB). The samples were shaken at 160°C to dissolve the polymer sample. All samples appeared to be soluble after overnight shaking. All samples were filtered through a 2  $\mu\text{m}$  stainless steel frit filter. Polystyrene standard was used for reference.

Differential scanning calorimetry and thermogravimetric analysis were performed using TA instrument systems model DSC 2920 and Hi-Res TGA 2950.

The wide angle X-ray powder diffraction (WAXD) was performed using Philips XLF ATPS XRD 1000.

### **3.8.2 Procedures**

**1,3-Cyclooctadiene** was prepared from 1,5-cyclooctadiene according to literature procedure.<sup>140</sup> 10.0 g (89.0 mmol) of potassium tert-butoxide is dissolved in 500 mL of dimethylsulfoxide. At room temperature, 200 mL (176 g, 1.63 mol) of 1,5-cyclooctadiene was then added. After 3 hours of heating at 70 °C, 150 mL of water was added to reaction mixture, followed by extraction with heptane and dried over sodium sulfate. Vacuum

distillation, b. p. 62~65 °C/105 mmHg, afforded 120 g (1.10 mol) of 1,3-cyclooctadiene (68 % yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 5.81 (d, *J* = 14Hz, 2H), 5.63 (m, 2H), 2.21(s, 4H), 1.50 (m, 4H)

**Bicyclo[4.2.0]oct-7-ene, 3** was prepared according to literature procedure.<sup>105</sup> 50 g (0.46 mol) of 1,3-cyclooctadiene, 2 mL of acetophenone and 500 mL of heptane was mixed in the photochemical reaction vessel equipped with water jacket and condenser. UV light (Hanovia medium pressure mercury vapor lamp, 450W, Ace Glass) was shined for 54 hours with maintaining reaction temperature at 80°C. Fractional distillation of reaction mixture with 30 cm long Vigreux column afforded 37 g (0.34 mol) of **3**. (b.p. 64~74°C/130 mmHg, 74 % yield) <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 6.13 (s, 2H), 2.86 (quintet, *J* = 4.3, 2H), 2.22~1.40 (m, 8H)

**Bicyclo[3.2.0]hept-6-ene, 4** was prepared according to literature procedure.<sup>104</sup> 5.0 g of 1,3-cycloheptadiene in 500 mL of pentane was placed in the photochemical reaction vessel equipped with water jacket and condenser. UV light (Hanovia medium pressure mercury vapor lamp, 450W, Ace Glass) was shined for 4 hours with steady reflux. Fractional distillation of reaction mixture with 30 cm long Vigreux column afforded 2.7 g (28 mmol) of **4**. (b.p. 96~97°C, 53 % yield) <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 5.87 (s, 2H), 3.16 (d, *J* = 6.6 Hz, 2H), 1.82~1.48 (m, 4H), 1.24~1.18 (m, 2H)

**[1,2-bis(diphenylphosphino)ethane]dichloronickel(II)** was prepared according to literature procedure.<sup>106</sup> A solution of 1,2-bis(diphenylphosphino)-ethane (2.0 g, 5.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was added dropwise to a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (1.2 g, 5.0 mmol) in ethanol (20 mL). The mixture was stirred for 30 min and then the dark orange crystals

collected by filtration, washed with diethyl ether and dried under vacuum. (yield 2.7 g, 100 %)

**[*N*-(3-*tert*-butylsalicylidene)-anilinato]-phenyl-triphenylphosphine nickel(II)** was synthesized modified procedure from literatures.<sup>119,141</sup> **(a) Ligand synthesis.** To a stirred solution of 3-*tert*-butylsalicylaldehyde (3.2 g, 18 mmol) in ethanol (5 mL), a solution of aniline (2.2 g, 23 mmol) in ethanol (10 mL) was added dropwise over a 5 minutes period at room temperature. The mixture was stirred for 24 hours and reaction mixture was concentrated in vacuo to afford a crude imine compound. Purification by column chromatography on silica gel using hexane/ethyl acetate (10/1) as eluent gave *N*-(3-*tert*-butylsalicylidene) aniline (3.9 g, 15 mmol) as a yellow oil in 86% yield. <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>): δ 8.63 (s, 1H), 7.44-6.86 (m, 8H), 1.47 (s, 9H) : **(b) Complex synthesis.** (*trans*[NiCl(Ph)(PPh<sub>3</sub>)] was prepared from Ni(PPh<sub>3</sub>)<sub>4</sub> and chlorobenzene.) To a stirred suspension of sodiumhydride (83 mg, 3.4 mmol) in THF, at room temperature solution of *N*-(3-*tert*-butylsalicylidene) aniline (0.38 g, 1.5 mmol) in THF (15 mL) was added dropwise over a 5 minutes period. The solution was stirred for 2 h. The resulting solution was filtered to remove excess sodiumhydride. After evaporating the solvent, sodium salt solid was formed. 25 mL of benzen and *trans*[NiCl(Ph)(PPh<sub>3</sub>)] (1.0 g, 1.4 mmol) was added to this sodium saltas. The mixture was stirred for 24 hours. After filtration, solvent was evaporated. The solid was recrystallized from a pentane solution at -40 °C to give a target complex (0.3 g, 0.5 mmol) as orange crystal in 34% yield. <sup>1</sup>H-NMR (300MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.20-7.84 (m, 28H), 0.91 (s, 9H)

$[(\text{ArN}=\text{C}(\text{H})-\text{C}(\text{H})=\text{NAr})]\text{Pd}(\text{CH}_3)\text{Cl}$  was prepared according to literature procedure.<sup>42</sup>  $[(\text{ArN}=\text{C}(\text{H})-\text{C}(\text{H})=\text{NAr})]$  ligand was prepared from glyoxal and diisopropylaniline.  $(\text{COD})\text{PdCH}_3\text{Cl}$  was prepared from  $(\text{COD})\text{PdCl}_2$  and tetramethyltin according to literature.<sup>142</sup> To the solution of  $(\text{COD})\text{PdCH}_3\text{Cl}$  (0.6 g, 2.2 mmol) in diethyl ether of 10 mL, the solution of ligand (0.86 g, 2.3 mmol) in diethyl ether was added at room temperature. Orange precipitation was formed shortly after mixing and mixture was stirred for 24 hours. The precipitation was then collected by filtration. Product was washed with diethyl ether and dried under vacuum. 1.06 g of orange powder was obtained. (1.99 mmol, 88 % yield)

**2,6-bis-[1-(2,6-dimethylphenylimino)ethyl]pyridine iron(II)chloride** was prepared according to literature procedure.<sup>49</sup> **(a) Ligand synthesis.** (Little modification was made on original procedure.) 2,6-diacetylpyridine (4.35 g, 24.5 mmol) and 2,6-diisopropylaniline (1.0 g, 6.1 mmol) were dissolved in 15 mL of dichloromethane. Three drops of formic acid and one scoop of sodium sulfate were then added to this solution. After stirring for 24 hours at room temperature. Sodium sulfate was removed by filtration and evaporation of solvent gave yellow solid. (0.76 g, 1.6 mmol, 26 % yield)  $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $J$  = 8.0Hz, 2H) 7.96(t, 1H) 7.18(m, 6H) 2.74(septet,  $J$  = 6.8Hz, 4H) 2.28(s, 6H) 1.18(m, 24H) : **(b) Complex synthesis.** Iron(II) chloride tetrahydrate (0.30 g, 1.5 mmol) and ligand (0.76 g, 1.6 mmol) were placed in reaction flask and then tetrahydrofran of 15 mL was charged to suspend. Reaction mixture turned dark blue immediately. After 24 hour of stirring at room temperature, diethylether was added slowly to be layered. Precipitation was collected by filtration, 0.44 g (0.72 mmol) of target material was obtained. (48 % yield)  $^1\text{H-NMR}$

(400MHz, CD<sub>2</sub>Cl<sub>2</sub>, all peaks are broadened)  $\delta$  81.94(2H) 14.95(4H) 5.32(12H) -6.37(12H) -11.02(2H) -24.03(4H) -37.89(6H)

**Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride** was prepared according to literature procedure.<sup>119</sup> To a stirred solution of *N*-(3-*tert*-butylsalicylidene)aniline (1.00 g, 3.95 mmol) in THF (40 mL) at -78 °C, a 2.0 M *n*-butyllithium cyclohexane solution (2.1 mL, 4.1 mmol) was added dropwise over a 5 minutes period. The solution was allowed to warm to room temperature and stirred for 2 hours. The resulting solution was added dropwise over a 30 minutes period to a stirred solution of ZrCl<sub>4</sub>·(THF)<sub>2</sub> (0.75 g, 2.0 mmol) in THF (40 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 24 hours. After removal of the solvent, the product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Filtration following removal of the volatile gave a yellow solid. The solid was recrystallized from a dichloromethane/diethyl ether (1/4) solution at -40 °C to give a target complex as fluorescent yellow solid (0.26 g, 0.39 mmol, 20% yield).

**Polymerization procedure in Table 3.3 (page 89)** : All manipulations are under nitrogen using Schlenk technique or dry-box.

**Run 1** : 1.00 g (9.24 mmol) of monomer **3** was dissolved in 4 ml of toluene at room temperature. 1 ml of 10 mmol/l nickel(II) acetylacetonate solution in toluene was added to this solution followed 1 ml of 100 mmol/l tris(perfluorophenyl)borane solution in toluene. After 24 hours stirring at room temperature, reaction mixture was poured into acidic methanol. No polymeric material was obtained.

**Run 2** : 1.00 g (9.24 mmol) of monomer **3** was dissolved in 3 ml of methylene chloride at room temperature. Methylaluminoxane (10 wt% in toluene) 1ml was added to this

solution, then, nickel complex 5 mg (9  $\mu$ mol) was added. After 20 hours, reaction mixture was poured into acidic methanol to precipitate polymer. Filtered and dried under vacuum yielded ~10 mg product.

**Run 3:** Nickel complex (5.4 mg, 8.3  $\mu$ mol) was weighed into Schlenk flask. Then 2.0 ml of toluene was added followed by adding 1.00 g (9.24 mmol) of monomer **3**. Bis(cyclooctadiene) nickel (6.6 mg, 0.024 mmol) was then added to this solution. After 24 hours stirring at room temperature, reaction mixture was poured into acidic methanol. No polymeric material was obtained.

**Run 4 :** 1.00 g (9.24 mmol) of monomer **3** was dissolved in 1 ml of toluene at room temperature. The solutions Palladium complex (10 mg, 2.0  $\mu$ mol) in 1 ml of toluene and tris(pentafluorophenyl)borane (20 mg, 4.0  $\mu$ mol) in 1 ml of toluene were then added to monomer solution at room temperature. After 24 hours stirring at room temperature, reaction mixture was poured into acidic methanol. No polymeric material was obtained.

**Run 5 :** 1.00 g (9.24 mmol) of monomer **3** was dissolved in 2 ml of toluene at room temperature. Methylaluminoxane (10 wt% in toluene) 2ml was added to this solution. After 48 hours of stirring, reaction mixture was poured into acidic methanol. Polymer was then filtered and dried under vacuum yielded trace amount of polymer.

**Run 6 :** 2.4 mg of zirconium monocyclopentadiene trichloride was weighed into Schlenk flask. Toluene of 1 ml was added, and then 10 ml of methylaluminoxane solution in toluene (10 wt%) was added. Monomer **3** (1.00 g, 9.24 mmol) was added. After 20 hours, reaction mixture was poured into acidic methanol. Precipitation was filtered and dried under vacuum, yielded 0.5 g of polymer. (50%)

**Polymerization procedure in Table 3.5 (page 105) :** All manipulations are under nitrogen using standard Schlenk technique or dry-box.

**Run 1 :** Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (1 mL of 10  $\mu\text{mol/mL}$  solution in toluene) was placed in Schlenk flask, then methylaluminoxane 1.7 M solution in toluene of 20 mL was added at room temperature. 1.00 g (9.24 mmol) of monomer **3** was added to this solution. After 24 hours of stirring at room temperature, hazy solution was poured into acidic methanol. Polymeric product was then washed, filtered and dried under vacuum. 0.64 g of **poly-3** was obtained as white powder. (64 % yield) High temperature (130°C) GPC analysis :  $M_w = 3,300$ ,  $M_n = 1,100$

**Run 2 :** Same procedure as Run 1 except for solvent, additional 20 mL of *o*-dichlorobenzene was used. (0.71 g, 71 % yield)

**Run 3 :** Same procedure as Run 1 except for amount of solvent, total of 40 mL of toluene was used. (0.46 g, 46 % yield)

**Run 4 (Copolymerization with ethylene) :** 1.00 g (9.24 mmol) of monomer **3** and 5 mL of toluene were placed in Schlenk flask. Ethylene was bubbled into this solution for 10 minutes at room temperature. Methylaluminoxane 1.7 M solution in toluene of 20 mL and following bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium (IV) dichloride (1 mL of 10  $\mu\text{mol/mL}$  solution in toluene) were added to this solution. After 10 minutes of stirring, reaction mixture was poured into acidic methanol. (1.62 g yield, 972 Kg/molZr·h activity) High temperature (130°C) GPC analysis :  $M_w = 8,200$ ,  $M_n = 3,600$

**Polymerization procedure in Table 3.7 (page 114)** : All manipulations are under nitrogen using standard Schlenk technique or dry-box. Literature procedures were modified and followed.

**Run 1** : Same as Run1 in Table 3.5.

**Run 2** : Methylaluminoxane 1.7 M solution in toluene of 3 mL was placed in Schlenk flask, and then bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (1 mL of 10  $\mu$ mol/mL solution in toluene) was then added at room temperature. 1.00 g (9.24 mmol) of monomer **3** was added to this solution. After 18 hours of stirring at room temperature, hazy solution was poured into acidic methanol. Polymeric product was then washed, filtered and dried under vacuum. 0.97 g of **poly-3** was obtained as white powder. (97 % yield) High temperature (130°C) GPC analysis :  $M_w = 219,000$ ,  $M_n = 141,000$

**Run 3**<sup>122</sup> : Methylaluminoxane 1.7 M solution in toluene of 3 mL was placed in Schlenk flask, then solvent and volatile trimethylaluminum were removed by 4 hours of vacuum. 3 mL of toluene was added to dissolve “dried” MAO, and bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (1 mL of 10.0  $\mu$ mol/mL solution in toluene) was then added at room temperature. Monomer **3** (1.00 g, 9.24 mmol) solution in 6 mL of toluene was added to this solution. After 18 hours of stirring at room temperature, hazy solution was poured into acidic methanol. Polymeric product was then washed, filtered and dried under vacuum. 0.83 g of **poly-3** was obtained as white powder. (83 % yield) High temperature (130°C) GPC analysis :  $M_w = 164,000$ ,  $M_n = 99,000$

**Run 4**<sup>130</sup> : Methylaluminoxane 1.7 M solution in toluene of 3 mL was placed in Schlenk flask, then 18  $\mu$ L of water was added to MAO solution and kept stirring for 10

minutes at room temperature. 0.84 g of pentafluorophenol in 3 mL of toluene was added and stirred for another 10 minutes. Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (1 mL of 10  $\mu$ mol/mL solution in toluene) was then added to this solution followed by monomer **3** (1.00 g, 9.24 mmol) solution in 3 mL of toluene was added to this solution. After 20 hours of stirring at room temperature, hazy solution was poured into acidic methanol. Polymeric product was then washed, filtered and dried under vacuum. 0.9 g of **poy-3** was obtained as white powder. (90 % yield) High temperature (130°C) GPC analysis :  $M_w = 7,400$ ,  $M_n = 2,100$

**Run 5**<sup>131</sup> : Triisobutylaluminum solution in toluene (1.0 M) of 1 mL was placed in Schlenk flask. 3 mL of toluene was added to this solution followed by bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (1 mL of 10  $\mu$ mol/mL solution in toluene). After 10 minutes of stirring at room temperature, 18 mg of triphenylmethyl tetrakis(pentafluorophenyl) borate in 2 mL of toluene was added, then monomer **3** (1.00 g, 9.24 mmol) solution in 3 mL of toluene was added. After 20 hours of stirring at room temperature, hazy solution was poured into acidic methanol. Polymeric product was then washed, filtered and dried under vacuum. 0.14 g of **poly-3** was obtained as white powder. (14 % yield) High temperature (130°C) GPC analysis :  $M_w = 2,400$ ,  $M_n = 700$

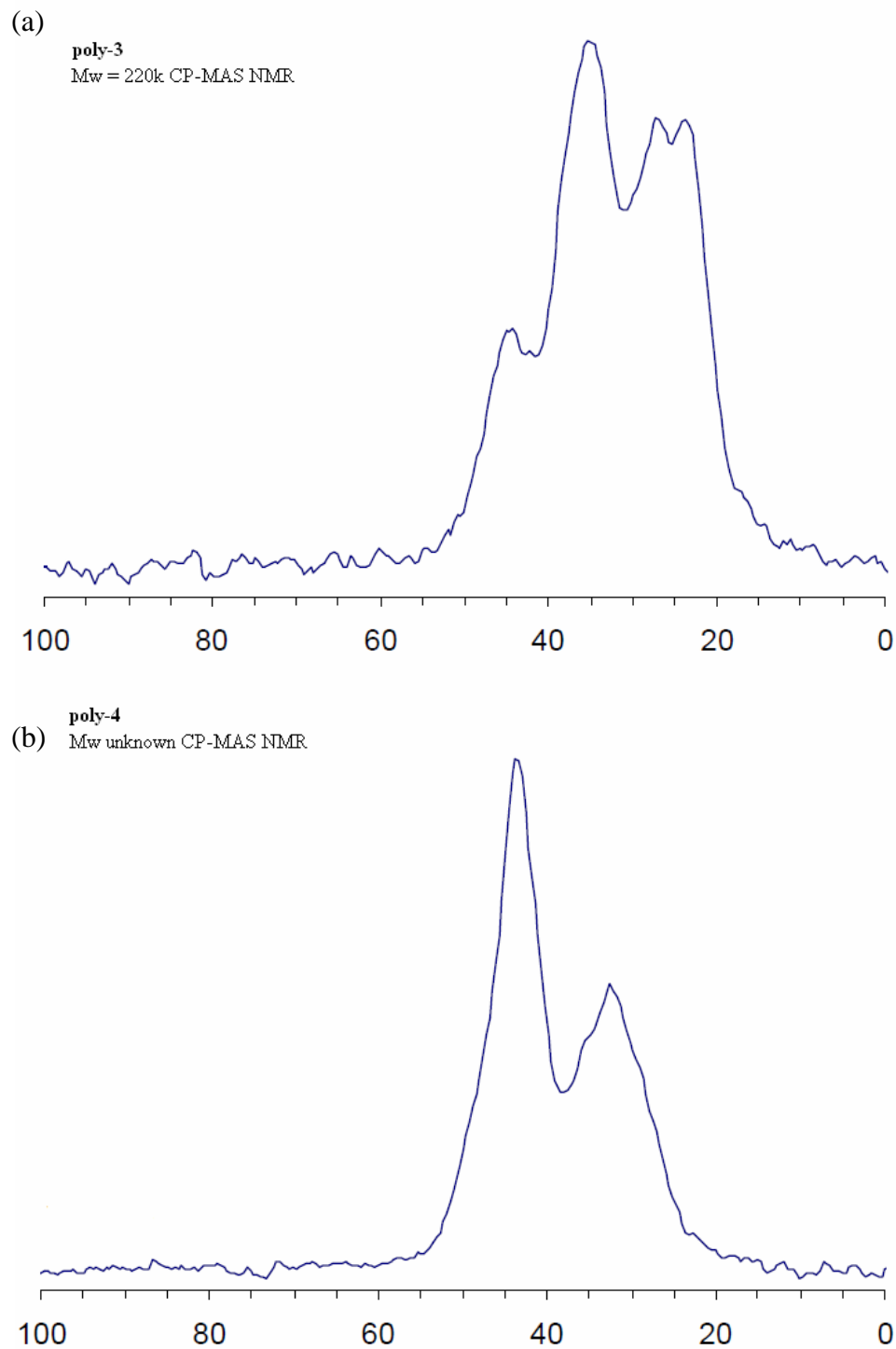
**Run 6**<sup>122</sup> : 0.42 mL of trioctylaluminum hexane solution (0.48M) was placed in Schlenk flask and hexane was removed under vacuum. After an addition of 4 mL of toluene, bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (1 mL of 10  $\mu$ mol/mL solution in toluene) was added. 5 mg of tris(pentafluorophenyl) borane in 3 mL of toluene was added, followed by addition of monomer **3** (1.00 g, 9.24 mmol) solution in 3 mL of

toluene. After 18 hours of stirring at room temperature, hazy solution was poured into acidic methanol. Only trace amount of polymeric material was obtained.

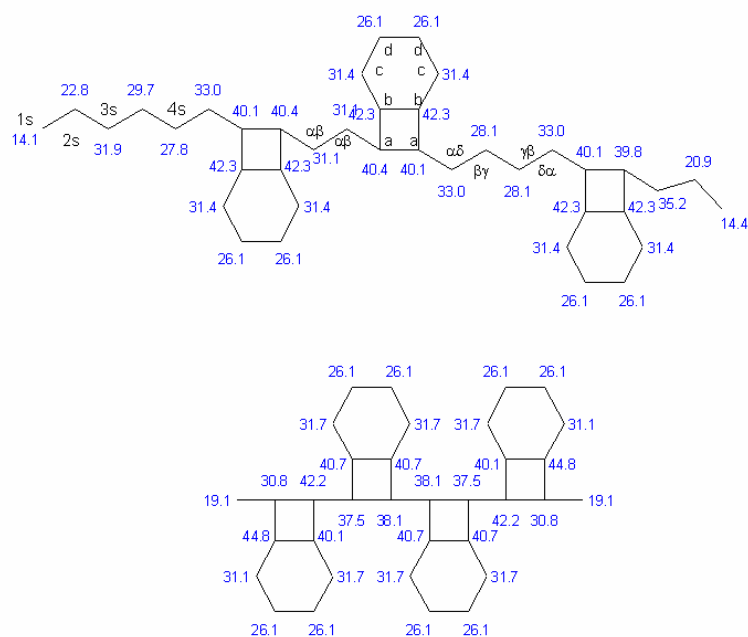
**Run 7** : At room temperature, 1.5 mL of triisobutylaluminum solution in toluene (1.0M) and 27  $\mu$ L of water were reacted in Schlenk flask with 2 mL of toluene. To this flask, 2 mL of methylaluminoxane toluene solution (1.7M) was added. Toluene solution of bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride (1 mL of 10  $\mu$ mol/mL solution in toluene) was added, then monomer **3** ( 1.00 g, 9.24 mmol) in 3.5 mL of toluene was added. After 22 hours of stirring at room temperature, hazy solution was poured into acidic methanol. Polymeric product was then washed, filtered and dried under vacuum. 0.86 g of **poy-3** was obtained as white powder. (86 % yield) High temperature (130°C) GPC analysis :  $M_w = 245,000$ ,  $M_n = 155,000$

**Polymrization of monomer 4** was performed same procedure as corresponding monomer **3** polymerization.

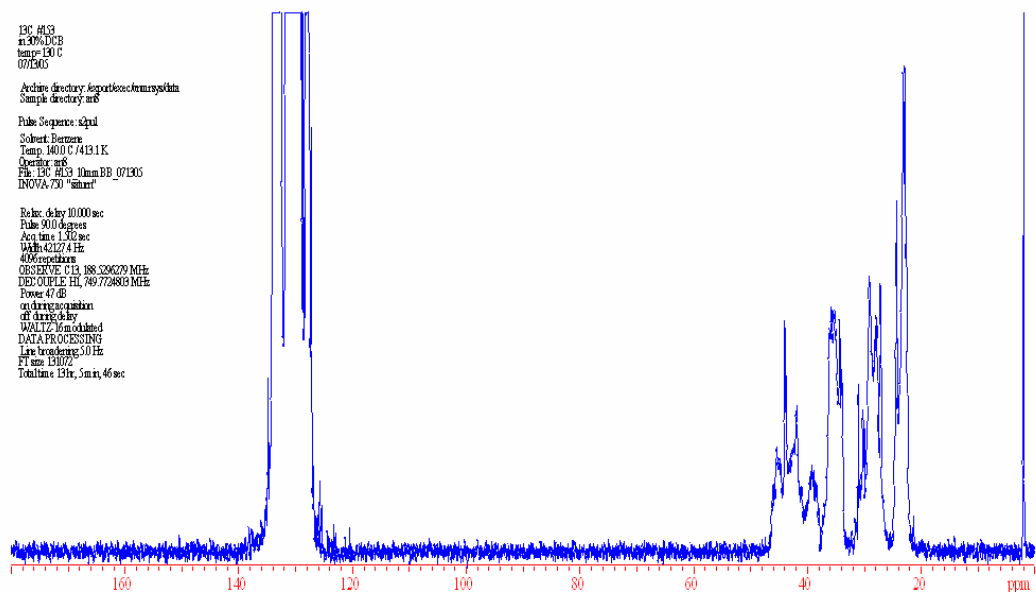
### 3.8.3 NMR Spectra (Selected Samples)



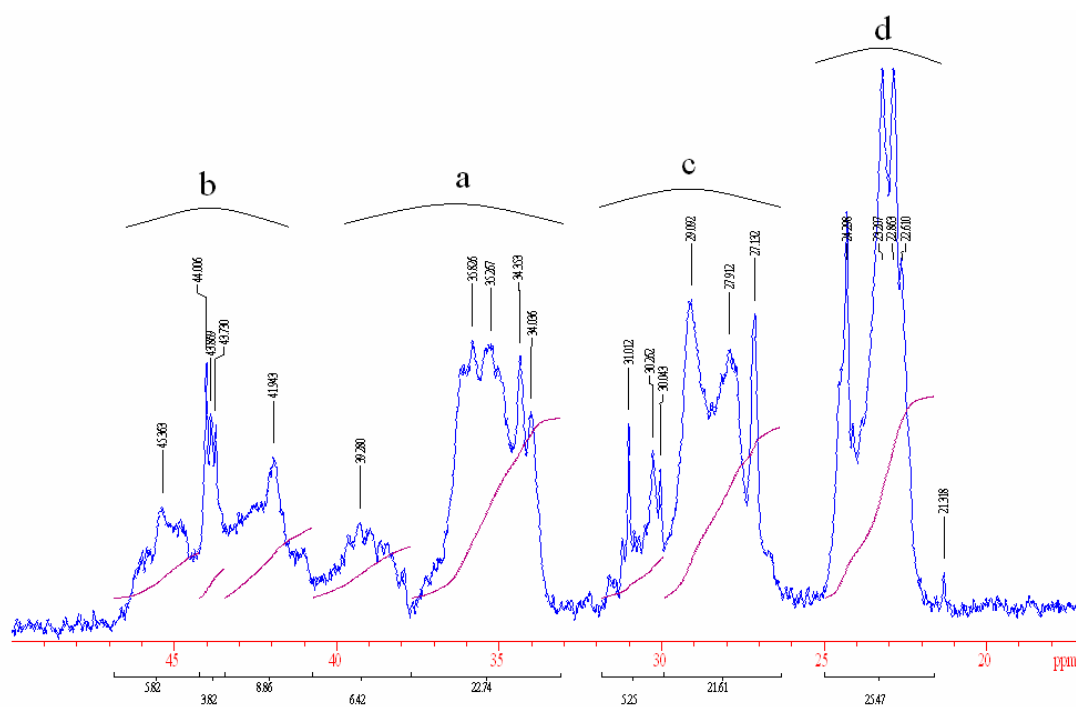
**Figure 3.36:** Solid state NMR spectra of (a) **poly-3** and (b) **poly-4**.



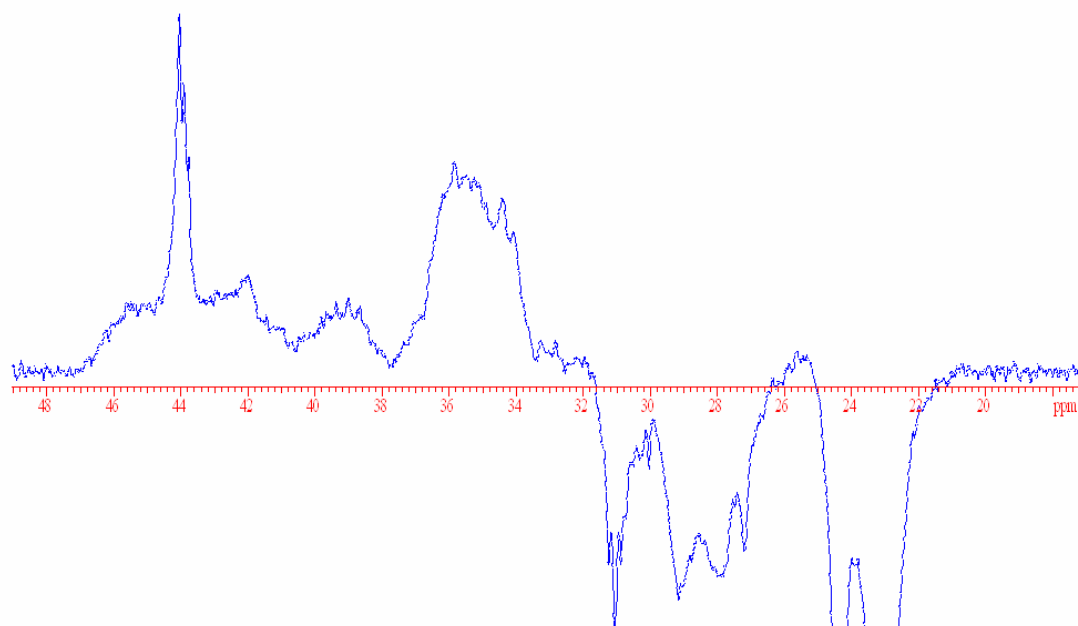
**Figure 3.37:** Estimated  $^{13}\text{C}$  chemical shift of **ethylene-3-copolymer** and **poly-3**.



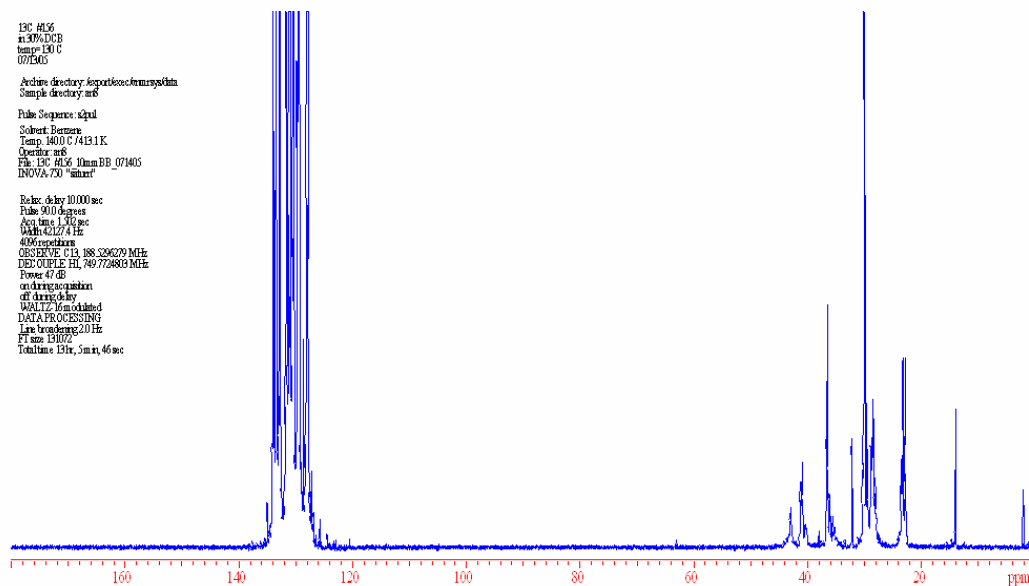
**Figure 3.38:**  $^{13}\text{C}$ -NMR spectrum of **poly-3** in *o*-DCB- $\text{d}_4$  at  $130^\circ$ .



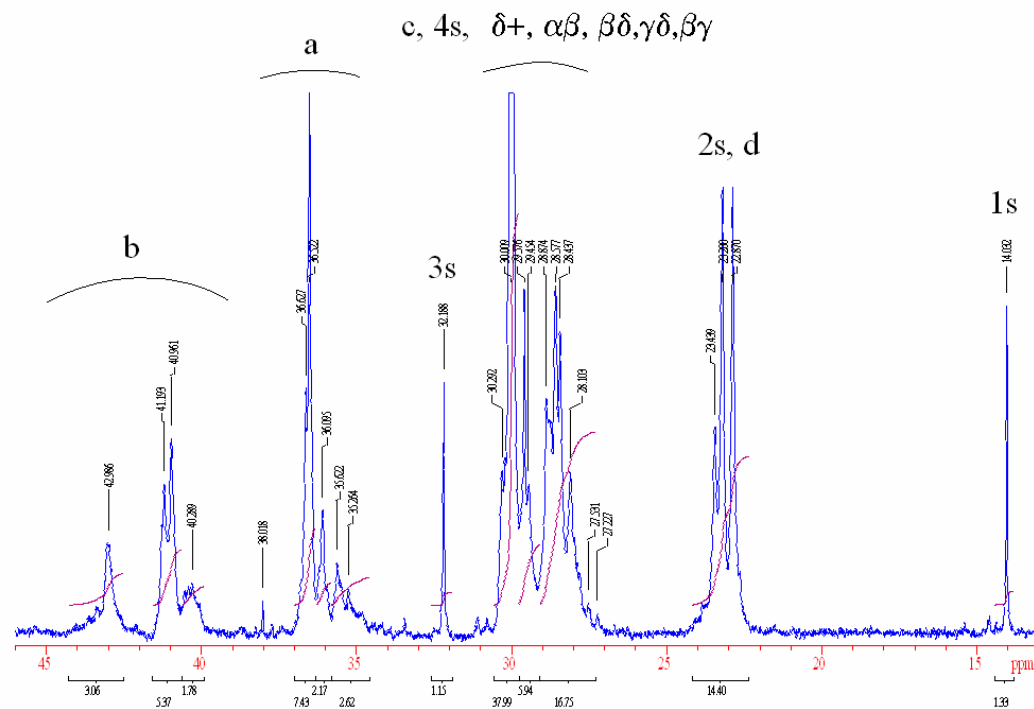
**Figure 3.39:**  $^{13}\text{C}$ -NMR spectrum of **poly-3** in *o*-DCB- $\text{d}_4$  at  $130^\circ$ .



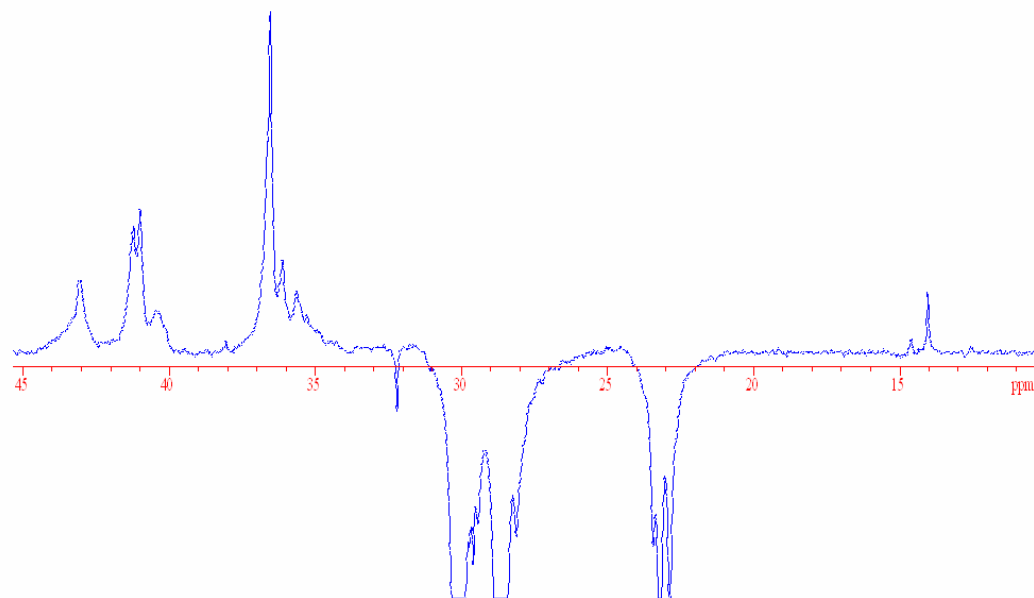
**Figure 3.40:** DEPT spectrum of **poly-3**.



**Figure 3.41:**  $^{13}\text{C}$ -NMR spectrum of ethylene-3-copolymer in *o*-DCB- $\text{d}_4$  at  $130^\circ$ .



**Figure 3.42:**  $^{13}\text{C}$ -NMR spectrum of ethylene-3-copolymer in *o*-DCB- $\text{d}_4$  at  $130^\circ$ .



**Figure 3.43:** DEPT spectrum of ethylene-3-copolymer.

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