Abstract

LEE, HYUN-SU. Asymmetric Polymerization initiated by Cationic Zirconocene Complexes possessing Chiral Counter Anions. (Under the Direction of Dr. Bruce M. Novak.)

Chiral induction in cationic polymerization was studied. New cocatalysts, Sodium *rac*-tris(tetra-chlorobenzenediolato)phosphate(V) and triphenylcarbenium *rac*-tris(tetra-chlorobenzenediolato)phosphate(V) for cationic zirconocene complexes were synthesized, respectively. The X-ray single crystal structure of triphenylcarbenium tris(tetra-chlorobenzenediolato)phosphate(V) showed that the crystal structure is a racemic mixture and there are four ion pairs in the asymmetric unit and eight ion pairs in the unit cell. The most interesting part is that the distribution of *delta*-isomers and *lambda*-isomers is equal in the unit cell, but the anionic isomers in the asymmetric unit are predominantly (75%) one isomer. Poly (*tert*-butyl vinyl ether) samples were synthesized by the initiating system of bis(cyclopentadienyl)dimethylzirconium and triphenylcarbenium tris(tetra-chlorobenzenediolato)phosphate(V) and by the initiating system of Sodium tris(tetra-chlorobenzenediolato)phosphate(V) and bis(cyclopentadienyl)zirconiumdichloride. The polymers exhibited reasonable yields, reasonable molecular weights, and reasonable molecular weight distributions, respectively and both are atactic polymers. These two systems did not control the stereoregularity of the polymers.

Chiral induction in coordination-insertion polymerization of carbodiimides was studied. New chiral cocatalysts, sodium *delta*-tris(tetra-chlorobenzenediolato)phosphate(V) and triphenylcarbenium *delta*-tris(tetra-chlorobenzenediolato)phosphate(V) for cationic zirconocene complexes possessing chiral counter anions were synthesized**,** respectively. The

catalytic system with bis(cyclopentadienyl)dimethylzirconium and trityl *rac*-TRISPHAT polymerized carbodiimide monomers and the resulting polymers have reasonable yields. The asymmetric carbodiimide polymerization by using cationic zirconocene complexes with *delta*-TRISPHAT anion yielded polymers. Unfortunately, we did not observe chiral counter anion with cationic catalytic site can generate single handed helical polymer in this polymerization system. Using ^{1}H-NMR spectroscopy, a mononuclear cationic complex [Cp_2ZrCH_3][*rac*-TRISPHAT] formed in catalytic system with $Cp_2Zr(CH_3)_2$ and [CPh_3][*rac*-TRISPHAT] was studied. Addition of carbodiimide monomers to the catalytic system and further ^{1}H-NMR spectroscopic monitoring showed that the catalytic system [Cp_2ZrCH_3][*rac*-TRISPHAT] initiates and polymerizes carbodiimide monomers.

A new chiral half-sandwich zirconium amidinate complex, $CpZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl) was synthesized. A new synthetic method of new dianionic C_2H_2–bridged Cp/guanidinate ligands for new chiral catalysts was discovered.

ASYMMETRIC POLYMERIZATION INITIATED BY CATIONIC ZIRCONOCENE COMPLEXES POSSESSING CHIRAL COUNTER ANIONS

by

Hyun-Su Lee

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

CHEMISTRY

Raleigh

2006

APPROVED BY:

_____	_____
Bruce M. Novak Chair of Advisory Committee	David A. Shultz
_____	_____
T. Brent Gunnoe	Alan E. Tonelli

Dedication

To my grandfather.

Acknowledgements

First of all, I must thank my advisor, Dr. Bruce M. Novak, who gave me the opportunity to work on challenging projects. The advice and support I received from him were invaluable. I am very grateful to Dr. David A. Shultz, Dr. T. Brent Gunnoe, and Dr. Alan E. Tonelli for serving on my advisory committee. I'd like to thank Dr. Gunnoe for making me interested in organometallic chemistry. I'd like to thank Dr. Mike H. Whangbo for helping me understand organometallic chemistry deeply.

I wish to extend my gratitude to the past and current members of the Novak Group, in particular to Dr. Gonglu Tian, Dr. Katsuyukin Tsuda, Dr. Yujie Lu, Yoko Aoyama, and Keitaro Seto for valuable discussions in chemistry and having fun during my years at NCSU. I would like to thank Dr. Lin He and Xinhui Lou for obtaining the MALDI spectrums of some compounds and Dr. Paul Boyle for the X-ray structures.

Finally, I'd like to thank my family for all of support. Especially I would like to thank my wife, Hyun-Hee Kim, for all of her love and support. This would not have been possible without you.

Table of Contents

Chapter II.

Asymmetric Cationic Polymerization initiated by Cationic Zirconocene Complexes possessing Chiral Counter Anions

Chapter III.

Helix-Sense Selective Polymerization of Carbodiimides by using Cationic Zirconocene Complexes possessing Chiral Counter Anions

Chapter IV.

Progress toward Chiral Zirconium Complexes for Asymmetric α-olefin Polymerization

List of Figures

List of Schemes

List of Tables

Chapter I.

General Overview of Generation of Single Handed Helical Polymers

1.1. Overview of chirality

A chiral molecule is one that has no center of symmetry and a non-superimposable mirror image.[1] The mirror image of a chiral molecule is called its enantiomer. Biological systems are generally chiral and the different chirality between two enantiomers can produce critically different pharmacological and biological effects.[2,3] Due to its important significance in biology, chirality has become more and more important not only in research interests, but also in many industries, such as the pharmaceutical industry, the food and beverage industry, agricultural chemicals, and electronics chemicals.[2,4-6]

1.1.1. Enantiomers and diastereomers

Two stereoisomers related as nonsuperimposable mirror images are called enantiomers, but if two or more stereoisomers with atoms connected in the same order are not related as mirror images, they are called diastereomers (Figure 1.1).[1,7] Enantiomers of a chiral molecule have the same physical properties, such as densities, melting and boiling points but diastereomers may have different physical and chemical properties. This difference between enantiomers and diastereomers is used to separate a chiral molecule from its enantiomer. Enantiomers have the same chemical properties in an achiral environment. However, their chemistry can substantially differ in a chiral environment. For example, a racemic mixture can react with an optically pure compound to produce a mixture of

diastereomers, which can be separated on the basis of solubility differences and then each enantiomer is recovered from diastereomeric derivatives by another chemical reaction.

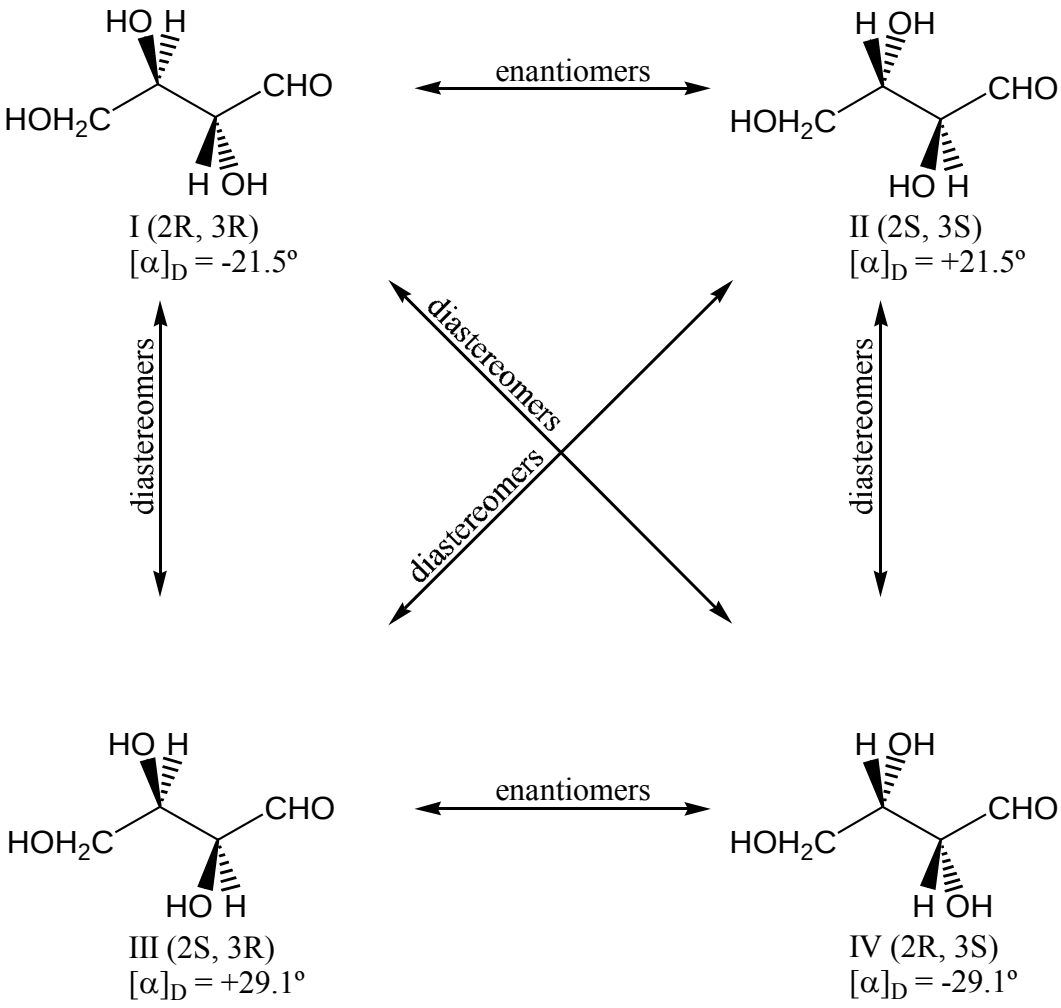


Figure 1.1. Configuration of enantiomers and diastereomers.

Although enantiomers have identical chemical properties in achiral environments, they differ in one physical property: enantiomers behave differently when interacting with plane polarized light. The separated enantiomers have an ability to rotate the plane of

polarized monochromatic light in equal but opposite directions.[8,9] A material with an excess of one enantiomer rotates plane-polarized light, so it is optically active. Conversely, achiral molecules or racemic mixtures with an enantiomeric excess of zero are optically inactive since they do not rotate plane-polarized light. Generally, a spectropolarimeter is used to measure optical activity of chiral substances at a variety of wavelengths. The angle of rotation α as a function of wavelength (λ) and at temperature T is recorded and the specific optical rotation $[\alpha]$ is calculated from the observed rotation α, the concentration c (g/100ml), and the length (l) of the polarimeter cell in decimeters according to equation 1.[1,8]

$$[\alpha]_{\lambda}^{T} = \frac{100\alpha}{cl} \qquad (1)$$

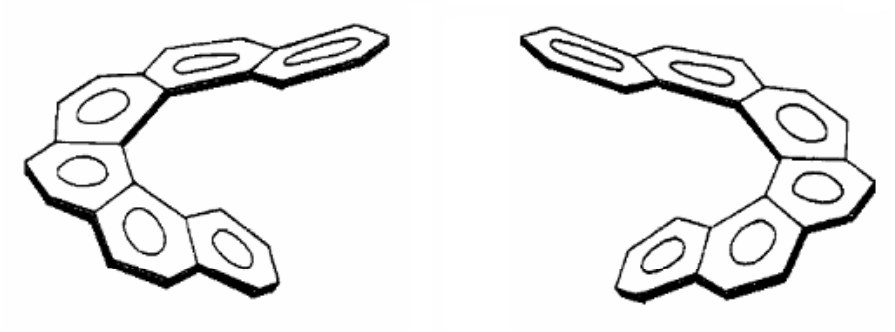
Optical activity is a property unique to chiral materials but the absence of optical rotation does not prove that no chiral structure is present. Enantiomeric excess (ee), equation 2, is another expression to show how pure a chiral material is.[10] From this equation, it can be seen that a racemic mixture (50% of each enantiomer) would have both a zero optical purity and enantiomeric excess of zero.

$$\%ee = \frac{[R]-[S]}{[R]+[S]} \times 100 \qquad (2)$$

1.1.2. Configurational and conformational chirality

There are two situations that may lead to chirality in molecules. First the molecule may have an atom that is asymmetrically substituted. The atom is a chiral center and the entire molecule is chiral. This leads to configurational chirality and optical activity. For

example, the chiral molecule (s)-(+)-2-octanol in Figure 1.3 contains a carbon atom bearing four different substituents and has optical activity.[11] On the other hand, a molecule may be chiral by virtue of its geometry or conformation. Some conformationally chiral molecules are chiral simply due to restricted rotation about a bond and have optical activity. Hexahelicene is an example of a conformationally chiral molecule and is optically active (Figure 1.2).[12-15]



(-)-Hexahelicene
$[\alpha]^{20}_{D} = -3640^{o}$

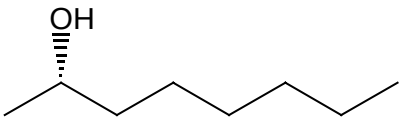
(+)-Hexahelicene
$[\alpha]^{20}_{D} = +3707^{o}$

Figure 1.2. Left-and right-handed forms of hexahelicene.

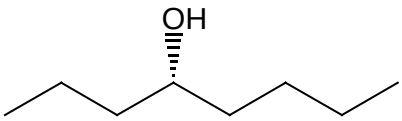
1.1.2.1. Configurational chirality

A configurationally chiral molecule can have optical activity. Several factors can influence the magnitude of the optical activity including the placement of the asymmetric atom within the molecule and the size of the substituents. When a series of structural isomers are compared the optical activity can change significantly depending on the placement of the chiral center. One example would be different optical activities of structural isomers of octanol depending on the relative sizes of the substituents. Substituents that are similar in size will lead to smaller observed optical activities while larger optical

activities are seen for molecules with chiral centers having the large ratio of molecular weights of the substituents (Figure 1.3).[11,16,17]



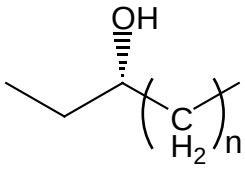
(S)-(+)-2-Octanol
$[\alpha]^{20}_{D}$ +9.76º (neat)



(S)-(+)-4-Octanol
$[\alpha]^{20}_{D}$ +0.57º (neat)

Figure 1.3. Structural isomers of octanol.

When a homologous series with increasing length of one of the substituents is compared, specific optical rotation can decrease since optical activities depend on the local region of the asymmetric center (Figure 1.4).[16]



n	3	7	11	14
$[\alpha]^{20}_{D}$ (neat)	+8.13º	+6.25º	+5.53º	+4.77º

Figure 1.4. Specific optical rotations for selected members of a homologous series.

Consequently, although compounds having asymmetrically substituted atoms whose substituents are very long chains are chiral, they may show zero specific optical rotations due to the manner in which optical activities are measured.[18] As molecular weight increases the specific optical rotation [α] may decrease since specific optical rotation is inversely proportional to the weight percent of the compound in solution.

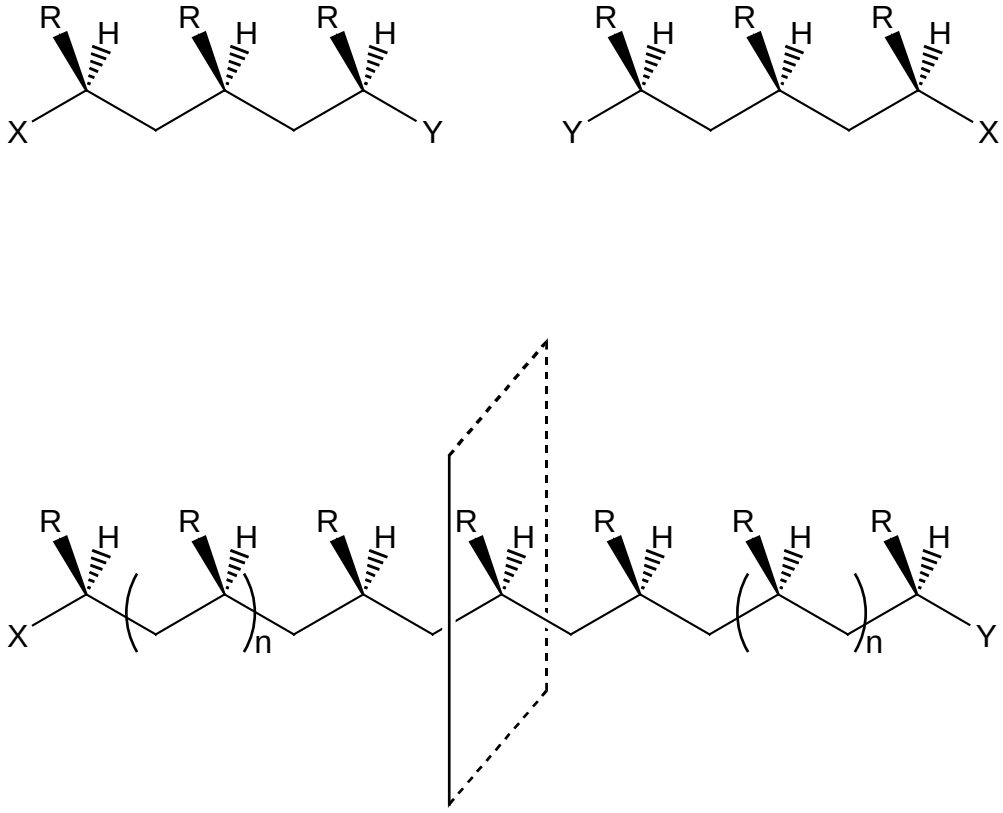
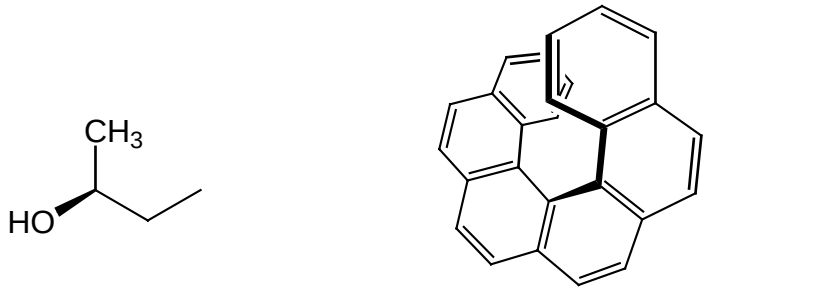


Figure 1.5. Comparison of the chirality of small chain molecules with stereocenters and high molecular weight polymers with stereocenters.

When stereoregular polymers with stereocenters are compared with short chain molecules possessing stereocenters, short chain molecules with stereocenters are chiral and have optical activity, high molecular weight polymers with stereocenters can be chiral molecules but do not have optical activity in most cases, because polymers have a pseudo-mirror plane that bisects each of the chiral centers and as the chain becomes infinite in length, these two groups effectively become equal to one another (Figure 1.5).[18,19]

1.1.2.2 Conformational chirality

The topics just discussed, placement of the chiral center, local region of the asymmetric atom, and molecular weight effects, apply only to configurationally chiral compounds. In a conformationally chiral compound there may be no chiral center because it is not necessary that there be an asymmetrically substituted atom. Thus placement and local region of the chiral center are incongruous with the concept of conformational chirality. Due to the nature of the chiral structure a conformationally asymmetric compound can have an optical activity that is much greater than a configurationally chiral compound (Figure 1.6).[14,20]



(S)-(+)-2-Butanol
$[\alpha]^{20}_{D}$ = +13º (neat)

(+)-Hexahelicene
$[\alpha]^{20}_{D}$ = +3707º (c = 0.08, $CHCl_3$)

Figure 1.6. Comparison of the specific optical rotations of a configurationally chiral molecule and a conformationally chiral molecule.

In addition, there is a more fundamental difference in the two types of chirality that is quite significant. The conformation of a molecule is dynamic and can be affected by such influences as light, heat, and pH.[21-23] In contrast, the configuration of a molecule is fixed and can only be changed via chemical means.

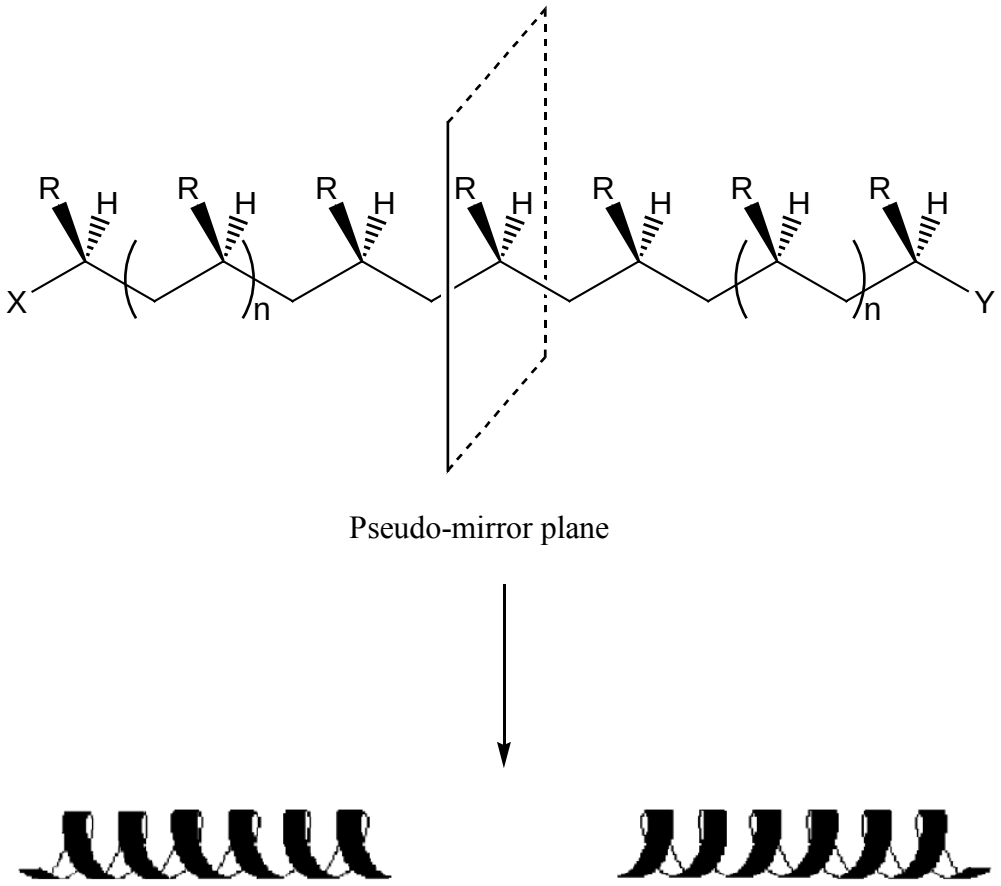


Figure 1.7. Stereoregular polymers adopting helical conformation to avoid steric hindrance between neighboring side groups.

Some high molecular weight polymers can have conformational chirality and optical activity. Stereoregular polymers with stereocenters may have a pseudo-mirror plane and do not have optical activity but stereoregular polymers can adopt helical conformations to avoid steric hindrance between neighboring side groups (Figure 1.7). For an example, isotactic polypropylene has a helical conformation and is a racemic mixture of helices in the solid

state.[24-27] If the stereoregular polymers with helical conformations have a preferred helical conformation, the polymers may have conformational chirality and optical activity. For an example, a single handed helical poly(triphenylmethyl methacrylate) has conformational chirality and optical activity ($[\alpha]_D$ = +384º).[28,29] The one-handed helical polymers exhibit high chiral recognition, which enables the resolution of many enantiomers when used as chiral stationary phases for HPLC.[29-32]

1.2. Overview of single handed helical polymers

Generally polymers exist in a variety of conformational forms ranging from randomly coiled chains to more spatially ordered structures. Due to steric hindrance between neighboring side groups or intermolecular interaction, the stereoregular polymers with regular internal rotational angles along the backbone can adopt helical conformations.

Some polypeptides can adopt helical conformations in the solid and solution states due to the presence of intermolecular and intramolecular hydrogen bonding, respectively.[33] Several synthetic polymer systems including polysilanes,[34,35] polyacetylenes,[22,23,36-40] poly(triarylmethyl methacrylates),[28,29,31] polyaldehyes,[41] polyisocyanides,[42-45] polyisocyanates,[43,46-50] and polycarbodiimides[51-56] are known to display a helical conformation in solution or the crystalline state. Highly isotactic and syndiotactic poly(α-olefins) can have a helical conformation in the solid state, such as isotactic poly(vinyl ethers)[57] and isotactic and syndiotactic polypropylenes,[24-27,58,59] and isotatic polyvinylcyclohexanes.[60-62]

As we discussed, there are several kinds of helical polymers, but single handed helical polymers are a few. The potential applications of single handed helical polymers are

many. The applications include molecular recognition (separation,[30,32,63-70] catalysis,[71-77] sensory function), optical data storage,[78,79] as molecular scaffolds for controlled alignment of functional groups or chromophores, and ordered molecular alignment in the solid phase such as that in liquid crystalline materials.[80] These applications make single handed helical polymers interesting for many synthetic polymer scientists.

1.2.1. Generation of single handed helical polymers

Helical polymers prepared from achiral monomers using optically inactive catalyst systems show no optical rotation because the product exists as a racemic mixture of left- and right-handed helices. In order to generate single handed helical polymers several strategies have been developed.

First, if a polymer is synthesized from an optically active monomer, and the polymer adopts the thermodynamically controlled conformation, a single handed helix can be isolated. For an example, Green and co-workers synthesized poly[(R)-1-deutero-n-hexylisocyanate] from the chiral monomer and the resulting polymer has a large preference for single handed helical sense caused cooperativity only by the pendant chiral group having a hydrogen and a deuterium. The chiral monomer has specific optical rotation of only -0.04º (neat), but the conformationally chiral helical polymer has a much larger specific optical rotation of +302º (in hexane).[46-50] Cooperativity refers to interaction between monomer units that allow single chiral perturbation in the polymer to influence the regional conformation of the polymer. The preparation of optically active polymer from a chiral monomer is sometimes inconvenient, because it requires a large amount of expensive chiral starting materials.

Second, the cooperativity of a chiral comonomer in polymers can influence these highly cooperative polymers to form a nearly single-handed helix. Green and coworkers synthesized copolymers from chiral isocyanate and achiral isocyanate monomers and have shown that the optical rotation of the copolymer can increase as the number of chiral monomers increases.[46-50] Novak and Lu synthesized the random copolymers of chiral carbodiimide and achiral carbodiimide monomers and have shown that the optical rotation increases for the copolymers as the percent of the chiral monomer decreases.[52,53,81]

The conversion of an effectively achiral polymer into an optically active, helical rod by use of a chiral chaperone can isolate a single handed helical polymer. (i.e., one molecule dictating the conformation of another molecule). Okamoto and coworkers reported poly((4-carboxypheny1)acetylene) by complexation with chiral amines leads to a single handed helix. This may be the first example of the prevailing helix formation of an achiral polymer ascribed to an acid-base interaction.[36-38,40] Novak and Schlitzer showed that using achiral polyguanidines and a chiral acid, chiral ion pairing interactions lead from a racemic mixture of helices to one of predominantly a single helix sense.[51]

A more attractive strategy is to polymerize achiral monomers with a chiral reaction environment. The helix-sense-selective polymerization of achiral monomers using chiral catalysts , chiral initiator, chiral counter ion, or chiral solvents yields kinetically controlled helical polymers, e.g., polyisocyanides,[44] poly(quinoxaline-2,3-diyl)s,[82,83] poly(trityl methacrylates),[28,29,31] poly(trityl methacylamides),[84] and polycarbodiimides.[52-56,81] We are interested in the helix-sense-selective polymerization of achiral monomers by using chiral reaction conditions.

1.2.2. Helix reversals and inversion barrier of racemization of single handed helical polymers from achiral monomers

Areas separating left- and right-handed helical segments are referred to as helix reversals (Figure 1.8). These reversals are at a higher energy than either the right- or left-handed helical regions, so higher temperature favors more reversals. This is apparent from polarimetry measurements of biased helices at various temperatures. There are fewer helix reversals at lower temperatures, so at lower temperatures higher rotations are observed.

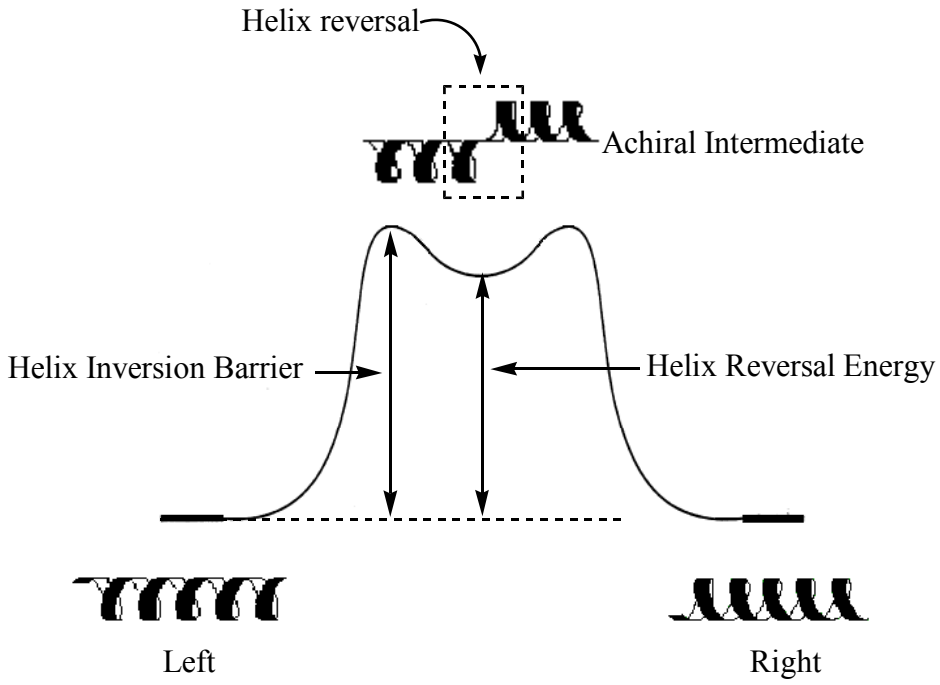


Figure 1.8. An energy diagram of helical inversion.[81,85,86]

The racemization of single handed helical polymers is involved in helix reversals that are in constant motion along the polymer backbone and are constantly being created and

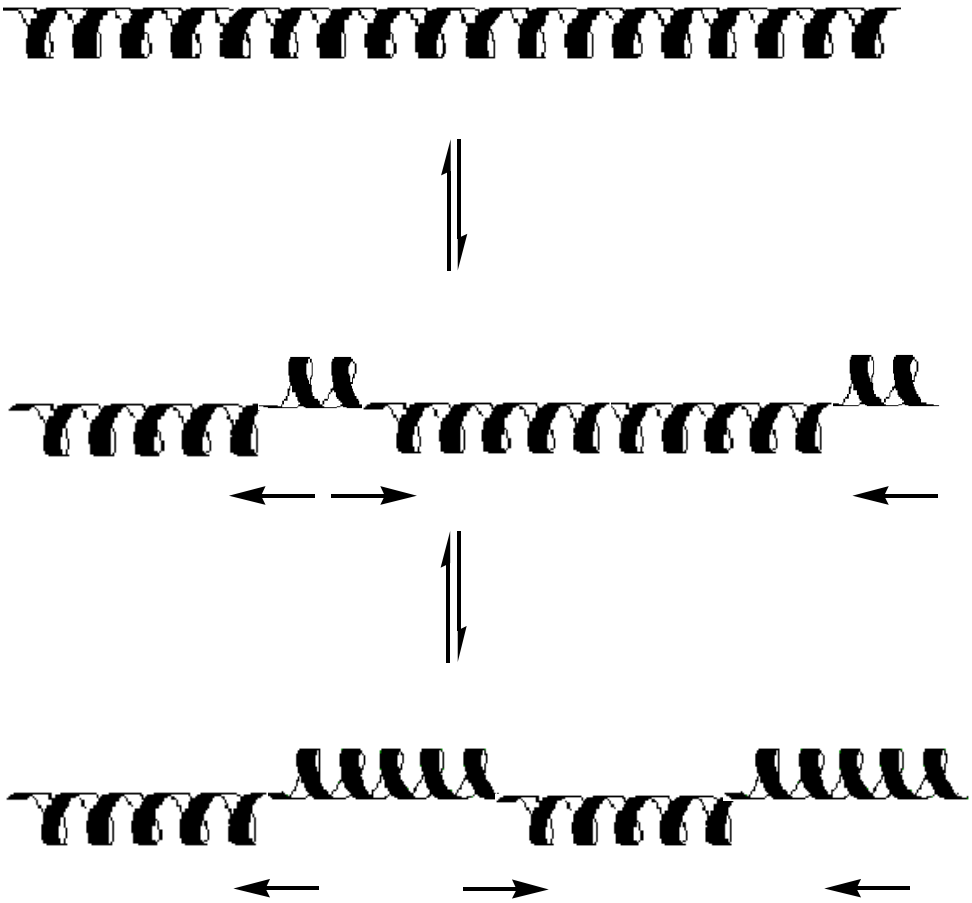


Figure 1.9. Racemization of a single handed helical polymer from achiral monomers.

destroyed (Figure 1.9). Helix reversals can be formed from a polymer chain by movement from the chain end or formation from the middle of the chain. Conversely, reversals can be removed in the reverse manner.

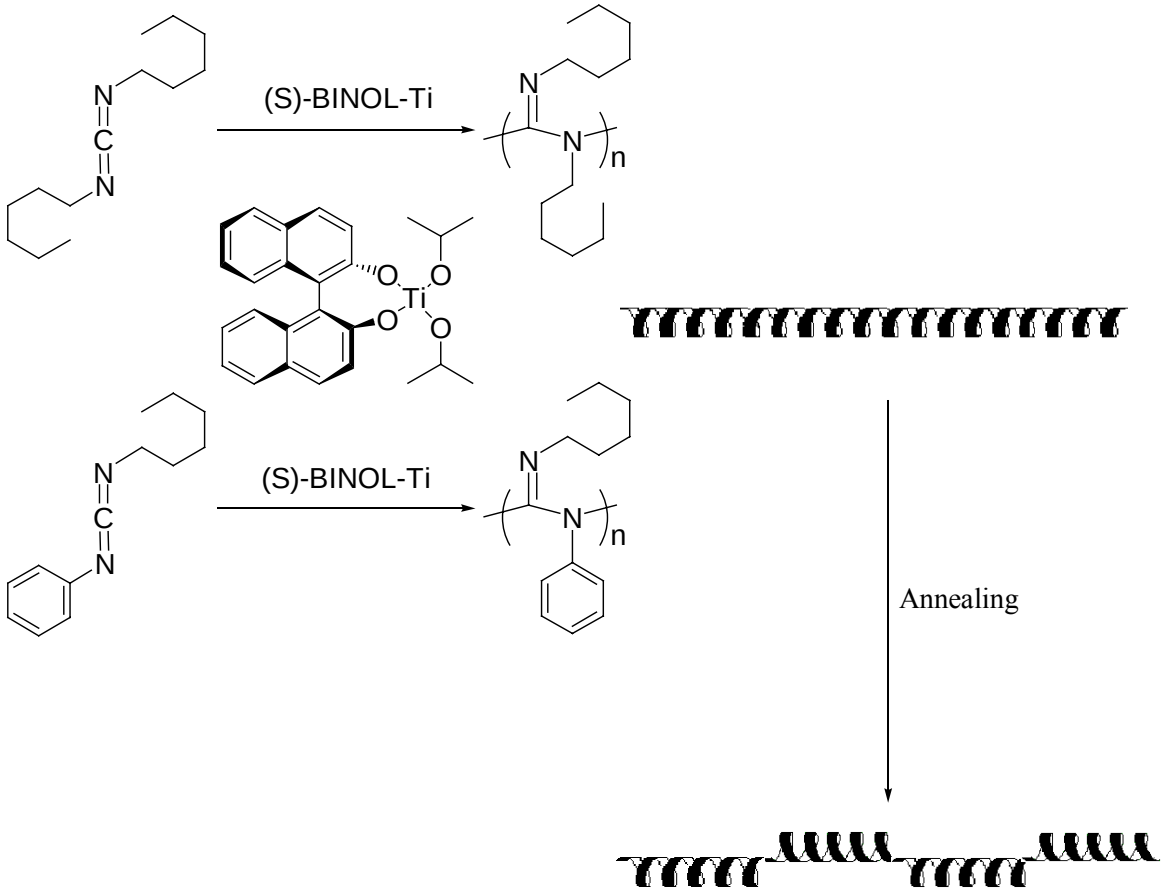
The entropy change of racemization of single handed helical polymer is always positive and the enthalpy change of racemization of single handed helical polymers could be positive since helix reversals are at a higher energy than either the right- or left-handed helical regions (equation 3).

$$\Delta G_{racemization} = \Delta H_{racemization} - T\Delta S_{racemization} \quad (3)$$

If $\Delta H < T\Delta S$, $\Delta G < 0$. The racemization of a single handed helical polymer is spontaneous and happens. If $\Delta H \geq T\Delta S$, $\Delta G \geq 0$, it means the racemization is not spontaneous or in equilibrium. So, if more bulky side chains are present or a lower temperature is used, then in a single handed helical polymer systems, $\Delta H > T\Delta S$, and racemization could be prevented.

The evidence for this lies in the racemization of single handed helical polymers from achiral monomers by chiral catalysts. Immediately upon polymerization with the chiral catalyst the polymers exist as a single-handed helix and the polymers have optical activity and during annealing the polymers lead to racemization and the optical rotation becomes zero (Scheme 1.1).

The kinetics of this racemization can reveal the helix inversion barrier of the polymer. The inversion barrier is the activation energy required to switch between a left- and right-handed helix. This barrier depends on several factors including the size and steric nature of the side chains and the inherent stiffness of the polymer backbone. A single-handed helical



Scheme 1.1. Helix sense selective polymerizations of achiral monomers by a chiral catalyst and subsequent racemization by annealing.

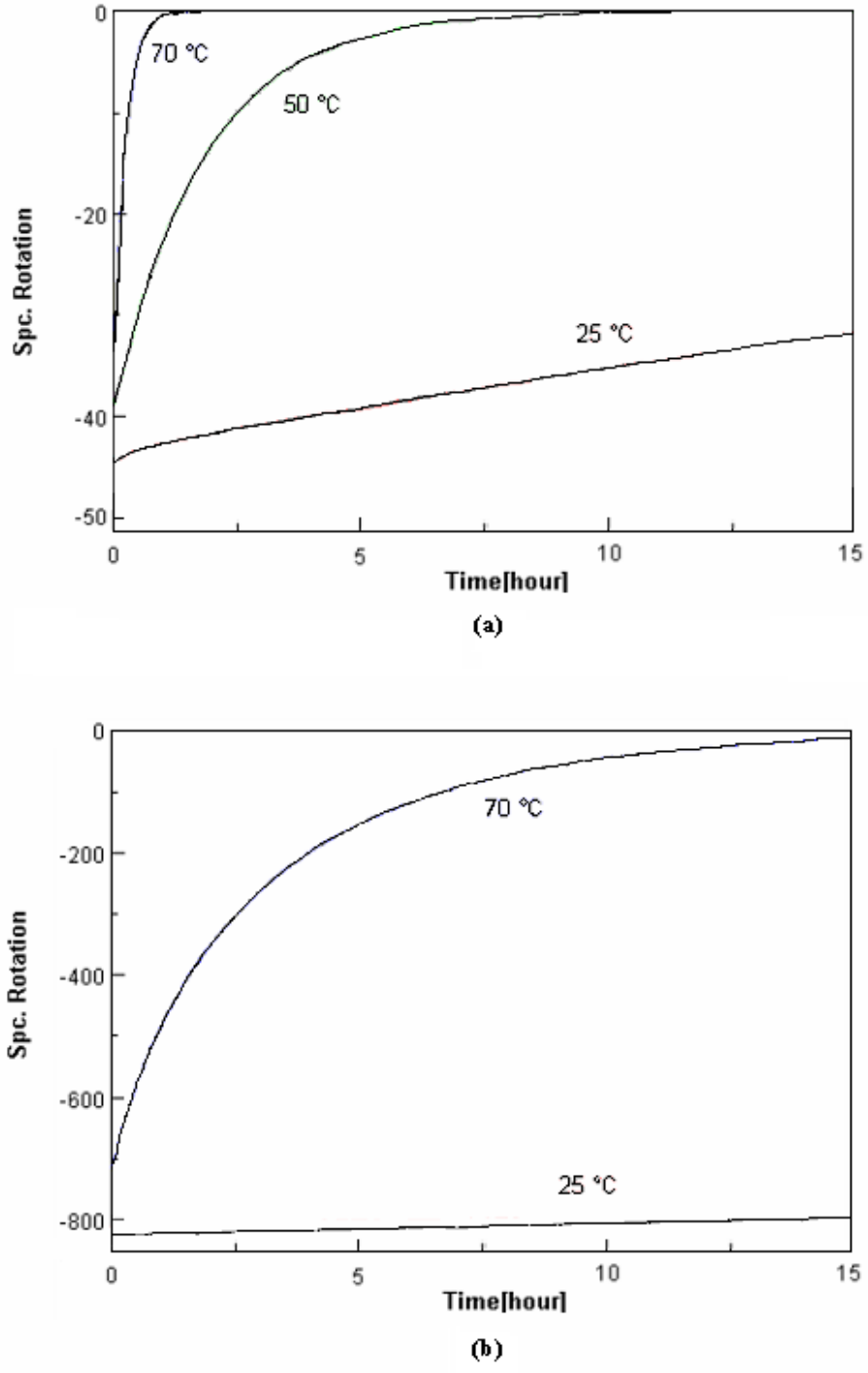


Figure 1.10. The specific rotation of poly(N,N'-di-hexylcarbodiimide) (a) and poly(N-(n-hexyl)-N'-phenylcarbodiimide) (b) as a function of time and annealing temperature.

polymer with a high inversion barrier will racemize slowly or not at all, while a lower inversion barrier leads to faster racemization.

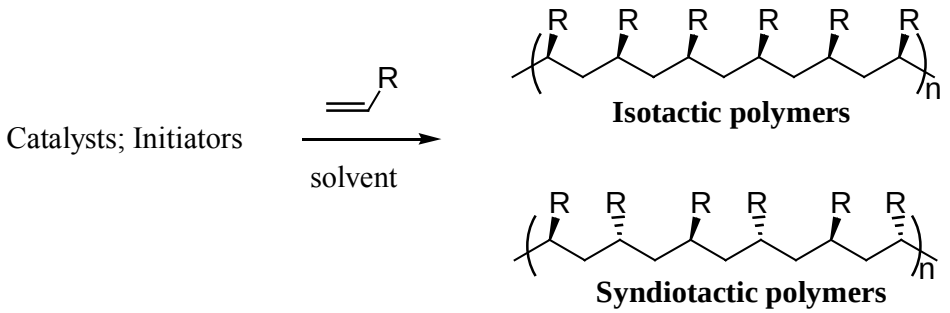
For an example, Tian and Lu synthesized single handed helical polycarbodiimides by chiral catalysts, and by measuring optical rotations as a function of time, discovered that the optical activity stabilities of both polymers were temperature dependent.[52,53,81] At higher temperatures, the optical activities of both polymers decrease and both polymers are racemized and the optical activites become zero (Figure 1.10). The polymers possessing more bulky side group are more slowly racemized. At the same annealing temperature, the racemization rate of poly(N,N'-di-hexylcarbodiimide) is faster than that of poly(N-(n-hexyl)-N'-phenylcarbodiimide), which indicates that helix inversion rates of polymers were affected by the size of side chains. Bulky groups slow the inversion of the helix conformation. By kinetic studies, the apparent activation energies for racemization are calculated to be 22.8 kcal and 25.6 kcal/mol for poly(N,N'-di-hexylcarbodiimide) and poly(N-(n-hexyl)-N'-phenylcarbodiimide), respectively.

Consequently, fluxional helices have low helix inversion barriers that allow frequent occurrences of helix reversals and lead to racemization. Non-fluxional helices have higher inversion barriers typically introduced by incorporating bulky side chains that hinder main chain bond rotation and have optical activity.

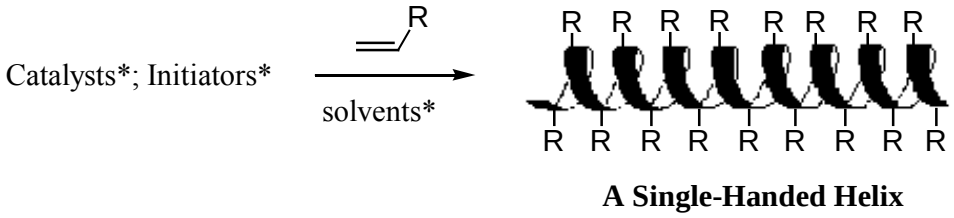
1.3. Generation of single handed helical polymers from achiral monomers

We are interested in the synthesis of single handed helical polymers from achiral monomers by using chiral reaction conditions. Here are the general considerations. First,

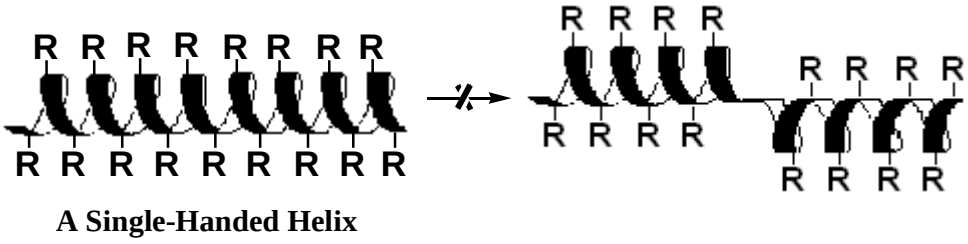
1. Configurational Control



2. Conformational Control



3. Prevention of Racemization through Main-chain Bond Rotations



Scheme 1.2. The synthesis of single handed helical polymers from achiral monomers by using chiral reaction conditions.

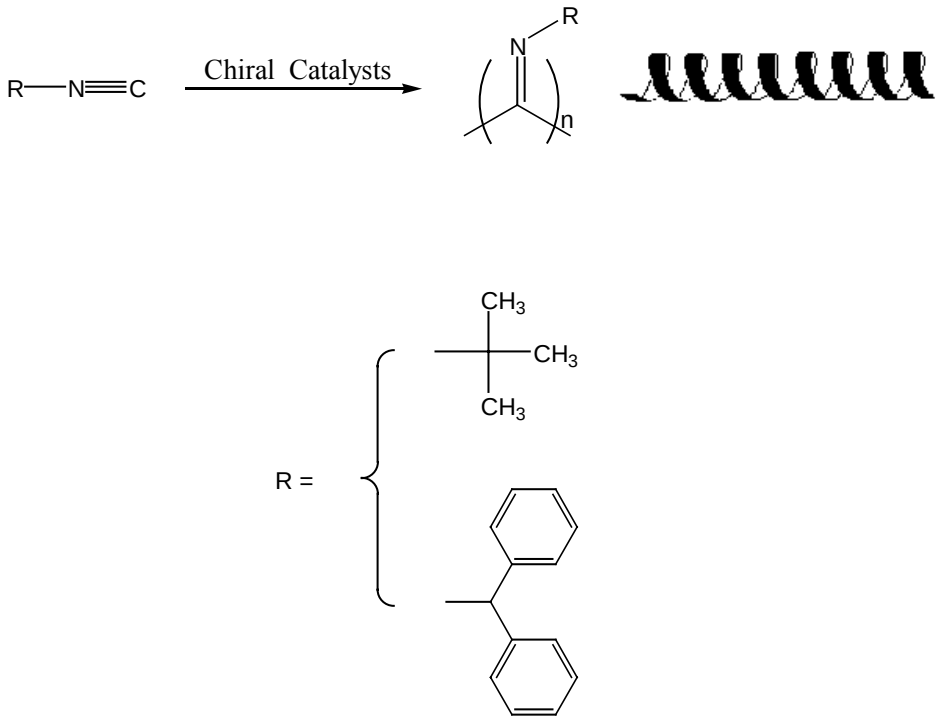
appropriate catalysts or initiators and monomers should yield highly stereoregular polymers and the polymers should have helical conformations. Second, the polymerization systems should possess chirality to select for a preferred helical sense. Last, bulky achiral monomers for the polymerization are needed since the bulky side groups of the polymers must be large enough to prevent racemization through main chain bond rotations (Scheme 1.2).

Several chiral polymerization conditions can be used for the generation of single handed helical polymers from achiral monomers including chiral catalysts, chiral initiators, chiral counter ions, or chiral solvents.

1.3.1. Chiral catalysts

There are several chiral environments for helix sense selective polymerization from achiral monomers. The most useful way is to use chiral catalysts since active catalytic sites for polymerization have chiral structures and the propagating catalytic sites always have chiral reaction environments during the polymerization and can lead to single handed helical polymers.

The first example would be helix-sense selective polymerizations of achiral isocyanides by chiral catalysts. Isocyanides can be polymerized using Lewis acids at low temperature, acid coated glass and a radical initiator, or nickel salts. More recently, well defined nickel(II) complexes were found to initiate the living polymerization of these monomers.[42,44,45,49,87] Polyisocyanides have a 4/1 helix and adopt a wormlike conformation in solution with relatively short persistence length, e.g., 30 Å for poly(1-phenylethyl isocyanide).[42,45] Poly(t-butyl isocyanide) also exists as a mixture of both left- and right-



Chiral Catalysts:

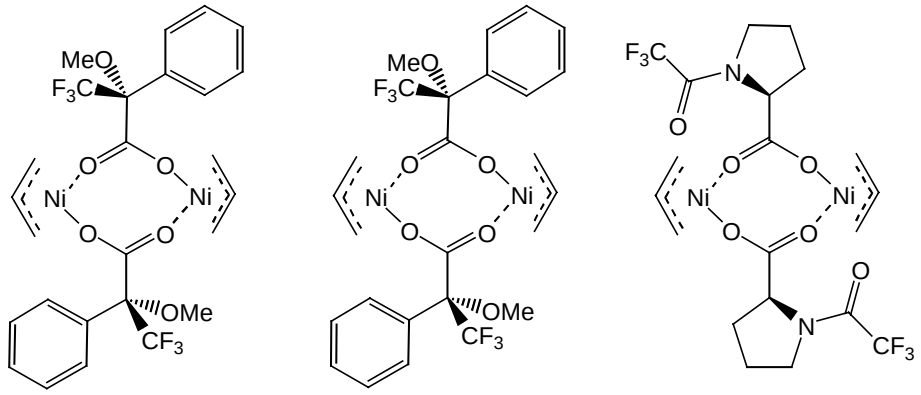


Figure 1.11. Enantioselective polymerization of achiral isocyanides by using chiral nikel (II) catalysts.

handed helices in solution. Helix sense selective polymerization of achiral isocyanides by using chiral nikel(II) catalysts yields optically active poly(t-butyl isocyanide) and poly(dipenylmethyl isocyanide) (Figure 1.11).[44] The optically active poly (t-butyl isocyanide) does not racemize at room temperature due to the high helical inversion barrier, i.e., ≥ 27 kcal/mol.

The next example would be helix sense selective polymerizations of achiral carbodiimides by chiral catalysts. The living polymerization of carbodiimides by titanium(IV) alkoxide, amidinate, and amide complexes has been developed.[88] Modification of the catalyst by attaching chiral ligands, such as (*S*)-binaphthnol (BINOL) and (*R*)-binaphthnol (BINOL), to the titanium center affords potential catalysts ((*S*)-BINOL-Ti) and ((*R*)-BINOL-Ti) (Figure 1.12).[52,53,81,89,90] The initiation of the polymerization proceeds through coordination-insertion of a carbodiimide into the isopropoxyl-titanium bond to afford an amidinate complex, which could then act as the propagating active sites in the polymerization process. During the polymerization, the chiral BINOL ligands lend chiral reaction environments to the active catalytic sites, which subsequently control the conformation of polymer chain to form single handed helical polycarbodiimides. Achiral N-(n-hexyl)-N'-phenylcarbodiimide monomers were polymerized with both chiral catalysts and the optical rotations of the resulting polymers catalyzed with ((*S*)-BINOL-Ti) and ((*R*)-BINOL-Ti) were measured to be $[\alpha]^{25}_{435}$ = -753° and +622°, (*c* = 0.2 in toluene), respectively (Figure 1.12).[52,53,81]

Consequently, chiral catalyst can generate single handed helical polymers from achiral monomers since polymerization active site have chiral environments formed by the chiral ligands.

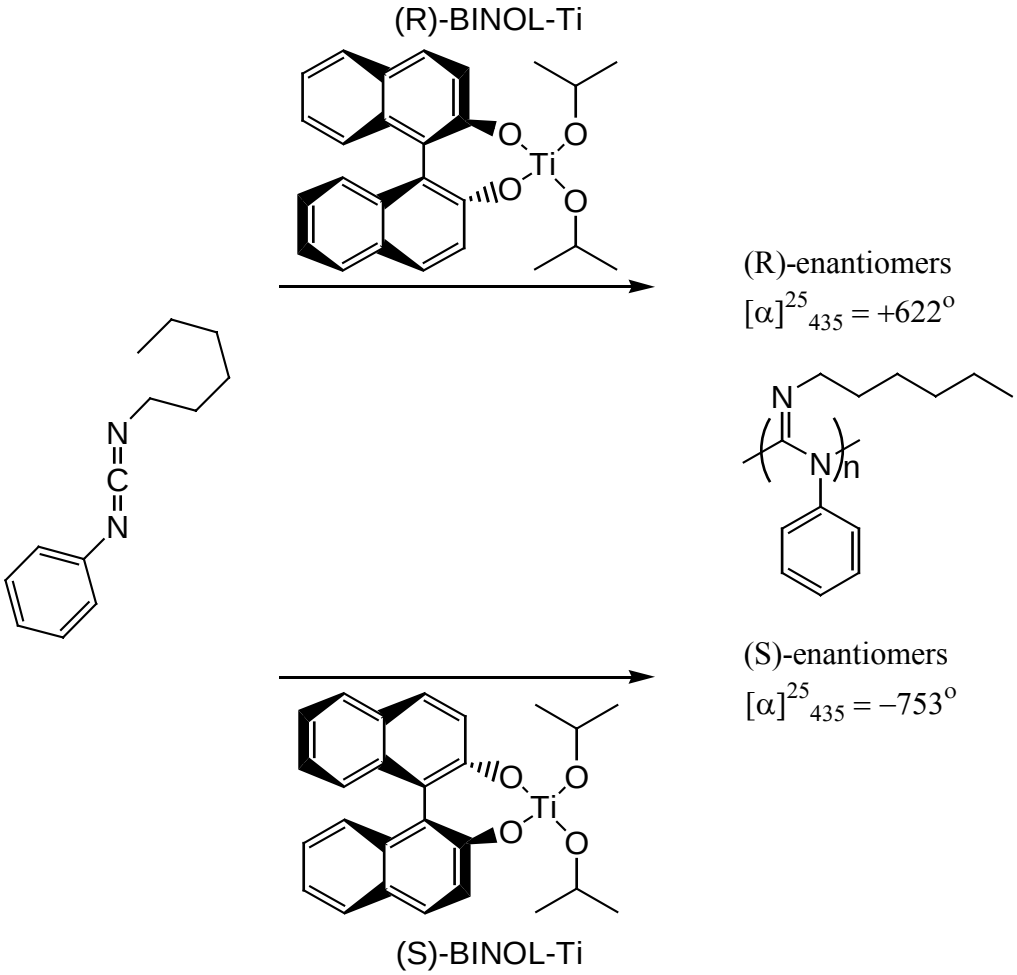


Figure 1.12. Helix-sense selective polymerization of achiral carbodiimides by using chiral titanium (IV) catalysts.

1.3.2. Chiral initiators and chiral counter ions

A single handed helical polymer can be generated by using chiral initiators or chiral counter ions. A good example is asymmetric anionic polymerization. Initiators for anionic polymerization consist of ion pairs such as an organic anion which initiates the monomer for anionic polymerization and a counter cation which always exists around the propagating sites and can stabilize propagating sites. When initiated by *n*-butyl lithium the bulky monomers induce a highly isotactic polymer such as isotactic poly(triphenylmethyl methacrylate).

Here are two kinds of chiral controlled systems for helix sense selective anionic polymerization (Figure 1.13). One is a chiral initiator controlled system which has chiral organic anion and can affect the initial stages for helical conformation such as lithium (*R*)-*N*-(1-phenylethyl)-anilide. The other is a chiral counter cation controlled system which has counter cation with chiral ligand and can form chiral reaction environment around the propagating sites, such as a complex of 9-fluorenyllithium with (-)-sparteine.

Helix sense selective anionic polymerization was reported by the Okamoto group.[28,29,31,64] Triphenylmethyl methacrylate monomers were used since the monomers induce a highly isotactic polymer when initiated by *n*-butyl lithium.[91,92] The polymerization was carried out using a complex of organolithum with a chiral ligand or using a chiral organolithum. When the two systems are compared, this ligand controlled system has been shown to lead to a high optical activity of the product since the chiral ligand coordinating to the counter cation always exist around the propagating site and creates a chiral reaction environment. But, this initiator controlled system gives relatively low selectivity since the chiral initiator will only affect the initial stages of helical conformation.

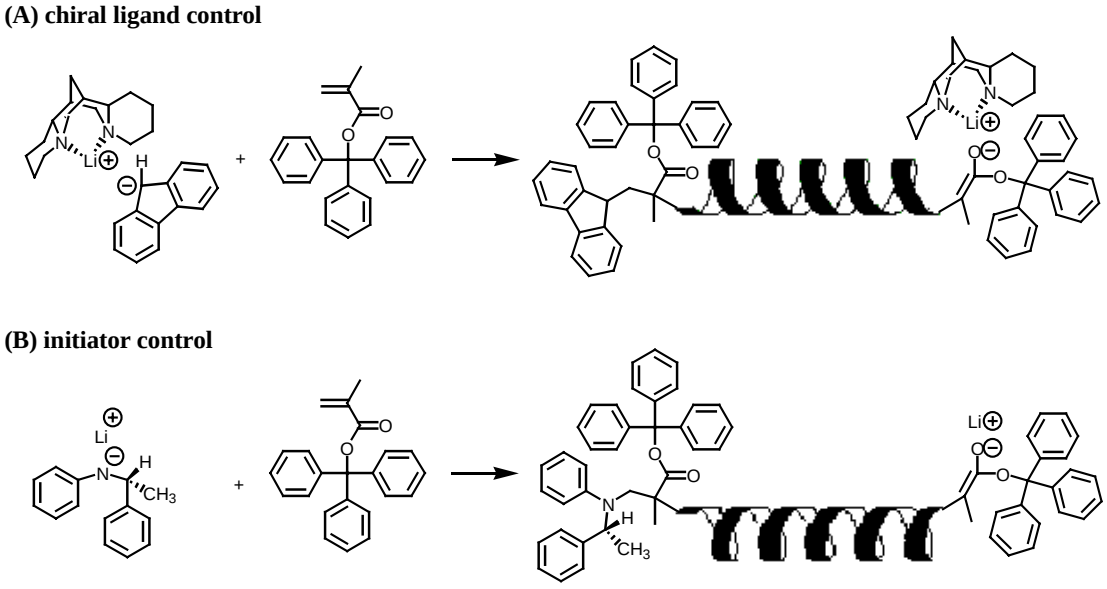


Figure 1.13. Helix-sense-selective anionic polymerization of TrMA: chiral ligand (A) and chiral initiator (B) control.[29,31]

Table 1.1. Optical Activity of Poly(TrMA) in the polymerization at -78˚C.[29,31]

control method	initiator	solvent	yield(%)	$[\alpha]_D$(deg)
Ligand control	FlLi-(-)-Sp	toluene	99	+384
Ligand control	n-BuLi-(-)-Sp	toluene	90	+245
Ligand control	n-BuLi-(-)-Sp	THF	100	+7
Initiator control	LiAn	toluene	73	-70
Initiator control	LiAn	THF	93	-82

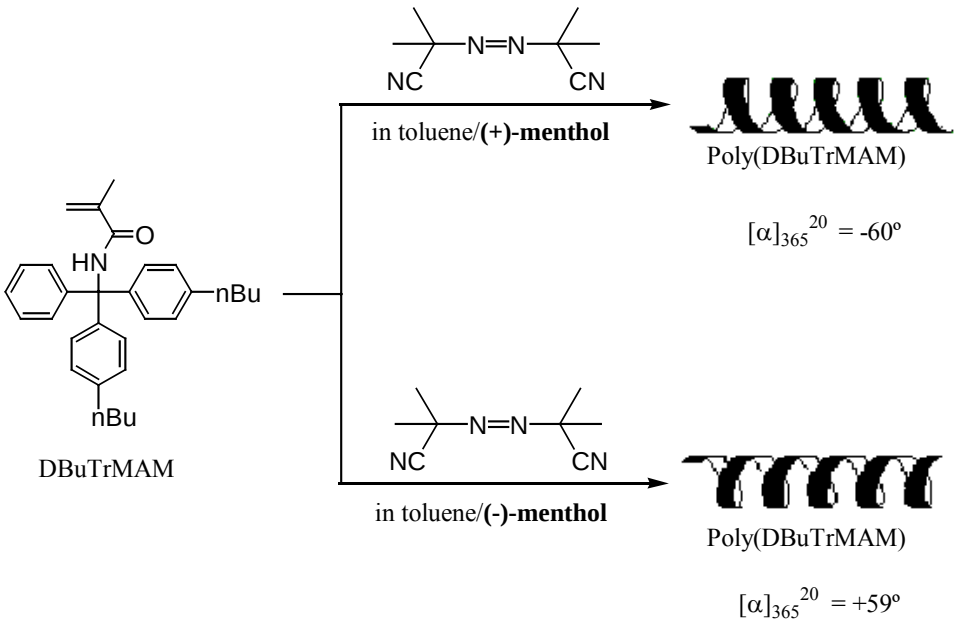
The chiral induction depends on the polarity of the solvent. The chiral counterion effects have been shown to lead to a higher helix-sense excess, i.e., higher optical activity of the product, in polymerizations run in less polar solvent (Table 1.1). This is consistent with shifting the ionic equilibrium toward tight ion pairs between propagating anions and counter cations.

Consequently, chiral counter cation controlled systems can lead to more predominant single handed helical polymers than chiral initiator controlled systems for helix sense selective anionic polymerization, since the propagating site of the chiral counter cation controlled system always has a chiral environment.

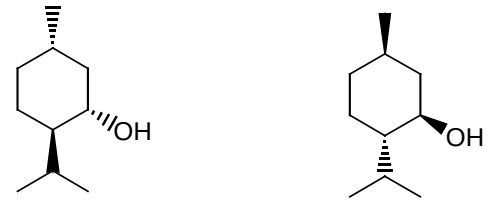
1.3.3. Chiral solvents

Generally it is hard to get single handed helical polymers by using radical polymerization, since the propagating site is a radical component and does not have chiral ligand or counterion effects in contrast with coordination-insertion and anionic polymerization.

There are a few examples for helix sense selective radical polymerizations. A few free-radical polymerization have been demonstrated to single handed helical polymers in the presence of chiral chain transfer agents such as (*R,R*)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminatocobalt(II).[93,94] One interesting method for asymmetry free radical polymerization is to use chiral solvents since chiral solvents can provide asymmetry reaction



Chiral solvent:



(+)-menthol **(-)-menthol**

Figure 1.14. Helix-sense selective radical polymerization by using chiral solvents.

environments.[95,96] Asymmetric radical polymerization of N-triphenylmethylmethacrylamides in chiral solvents leading to highly isotactic single handed helical polymers has been reported.[84] This monomer gave almost perfectly isotactic polymers when polymerized with radical initiator such as azobis(isobutyronitrile) (AIBN). The polymerization of DBuTrMAM in an optically active solvent, (-)- or (+)-menthol, afforded the optically active polymers having a prevailing one-handed helical structure (Figure 1.14).

1.4. Overall goals of the research

We are interested in syntheses of single handed helical polymers from achiral monomers using chiral polymerization systems.

The first area in this research is to develop new asymmetric polymerization systems by using chiral counter anions for asymmetry polymerization and generation of single handed helical polymers. The first interesting area is asymmetric cationic polymerizations from achiral vinyl ether monomers by using cationic zirconocene complexes possessing chiral counter anions. Second, we are interested in helix sense selective polymerization from achiral carbodiimide monomers by using cationic zirconocene complexes possessing chiral counter anions. Lastly, we are interested in synthesis of chiral zirconium complexes for asymmetry coordination-insertion polymerization of α-olefins and generation of single handed helical poly α-olefins.

Overall our research goals are to discover new chiral systems for asymmetric polymerization of achiral monomers and to synthesize new single handed helical polymers.

1.5. References

1. Carey, F. A., *Organic Chemistry, Fourth Edition*. McGraw-Hill Higher Education: 2000.
2. Challener, C. A., *Chiral Drugs*. Ashgate, Burlington: 2001.
3. Cabedo, N.; Andreu, I.; Arellano, M. C. R.; Chagraoui, A.; Serrano, A.; Bermejo, A.; Protais, P.; Cortes, D., *J. Med. Chem.* **2001,** 44, 1794-1801.
4. Rouhi, A. M., *Chemical & Engineering News* **2003,** 81, 56-61.
5. Rouhi, A. M., *Chemical & Engineering News* **2002,** 80, 43-50.
6. Stinson, S. C., *Chemical & Engineering News* **2001,** 79, 45-57.
7. Edin, M.; Bäckvall, J.; Córdova, A., *Tetrahedron Letters* **2004,** 45, 7697-7701.
8. Schirier, P.; Bernreuther, A.; Huffer, M., *Analysis of Chiral Organic Molecules: methodology and applications*. Walter de Gruyter, New York: 1995.
9. Carey, F. A.; Sunberg, J., *Advanced Organic Chemistry, Fourth Edition*. Kluwer Academic Plenum Publisher, New York: 2001.
10. March, J., *Advanced Organic Chemistry*. Wiley-Interscience, New York: 1992.
11. Pickard, R. H.; Kenyon, J., *J. Chem. Soc., Trans.* **1911,** 99, 45-72.
12. Lightner, D. A.; Hefelfinger, D. T.; Powers, T. W.; Frank, G. W.; Trueblood, K. N., *J. Am. Chem. Soc.* **1972,** 94, 3492-3497. .
13. Newman, P.; Rutkin, P.; Mislow, K., *J. Am. Chem. Soc.* **1958,** 80, 465-473.
14. Newman, M. S.; Lednicer, D., *J. Am. Chem. Soc.* **1956,** 78, 4765-4770.
15. Newman, M. S.; Darlak, R. S.; Tsai, L. L., *J. Am. Chem. Soc.* **1967,** 89, 6191-6193.
16. Pickard, R. H.; Kenyon, J., *J. Chem. Soc., Trans.* **1913,** 103, 1923-1959.
17. Levene, P. A.; Haller, H. L., *J. Biol. Chem.* **1929,** 83, 579-589.
18. Wulff, G., *Angew. Chem. Int. Ed. Engl.* **1989,** 28, 21-37.

19. Novak, B. M., *Organic Polymers Chemistry: A Primer*. 1995.

20. Loudon, G. M., *Organic Chemistry*. Addison-Wesley: Reading, MA: 1983.

21. Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M., *Chem. Rev.* **2001,** 101, (12), 4039-4070.

22. Morino, K.; Maeda, K.; Yashima, E., *Macromolecules* **2003,** 36, (5), 1480-1486.

23. Miyagawa, T.; Furuko, A.; Maeda, K.; Katagiri, H.; Furusho, Y.; Yashima, E., *J. Am. Chem. Soc.* **2005,** 127 (14), 5018 -5019.

24. Brückner, S.; Meille, S. V., *Nature* **1989,** 340, 455-457.

25. Meille, S. V.; Ferro, D. R.; Bruckner, S.; Lovinger, A. J.; Paddenl, F. J., *Macromolecules* **1994,** 27, 2615-2622.

26. Hirosea, M.; Yamamotoa, T.; Naikib, M., *Computational and Theoretical Polymer Science* **2000,** 10 345–353.

27. Auriemma, F.; Rosa, C. D.; Boscato, T.; Corradini, P., *Macromolecules* **2001,** 34, 4815-4826.

28. Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H., *J. Am. Chem. Soc.* **1979,** 101, 4763-4765.

29. Okamoto, Y.; Nakano, T., *Chem. Rev.* **1994,** 94, 349-372.

30. Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H., *J. Am. Chem. Soc.* **1981,** 103, 6971-6973.

31. Nakano, T.; Okamoto, Y., *Chem. Rev.* **2001,** 101, 4013-4038.

32. Yuki, H.; Okamoto, Y.; Okamoto, I., *J. Am. Chem. Soc.* **1980,** 102, 6356-6358.

33. McColl, I. H.; Blanch, E. W.; Hecht, L.; Barron, L. D., *J. Am. Chem. Soc.* **2004,** 126, 8181-8188.

34. Frey, H.; Moeller, M.; Matyjaszewski, K., *Macromolecules* **1994,** 27, 1814-818.

35. Fujiki, M., *J. Am. Chem. Soc.* **1994,** 116, 11976-11981.

36. Yashima, E.; Nimura, T.; Matsushima, T.; Okamoto, Y., *J. Am. Chem. Soc.* **1996,** 118, 9800 - 9801.

37. Yashima, E.; Matsushima, T.; Okamoto, Y., *J. Am. Chem. Soc.* **1997,** 119, 6345 - 6359.

38. Yashima, E.; Matsushima, T.; Okamoto, Y., *J. Am. Chem. Soc.* **1995,** 117, 11596-11597.

39. Onouchi, H.; Kashiwagi, D.; Hayashi, K.; Maeda, K.; Yashima, E., *Macromolecules* **2004,** 37, 5495 - 5503.

40. Maeda, K.; Morino, K.; Okamoto, Y.; Sato, T.; Yashima, E., *J. Am. Chem. Soc.* **2004,** 126, 4329 - 4342.

41. Ute, K.; Hirose, K.; Kashimoto, H.; Hatada, K.; Vogl, O., *J. Am. Chem. Soc.* **1991,** 113, 6305-6306.

42. Drenth, W.; Nolte, R. J. M., *Acc. Chem. Res.* **1979,** 12, (1), 30-35.

43. Goodman, M.; Chen, S., *Macromolecules* **1970,** 3, 398-402.

44. Deming, T. J.; Novak, B. M., *J. Am. Chem. Soc.* **1992,** 114, (20), 7926-7927.

45. Nolte, R. J. M.; Beijnen, A. J. M. V.; Drenth, W., *J. Am. Chem. Soc.* **1974,** 96, (18), 5932-5933.

46. Green, M. M.; Reidy, M. P.; Johnson, R. D.; Darling, G.; O'Leary, D. J.; Willson, G., *J. Am. Chem. Soc.* **1989,** 111, 6452-6454.

47. Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S., *Science* **1995,** 268, 1860-1866.

48. Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V., *Angew. Chem. Int. Ed.* **1999,** 38, 3138-3154.

49. Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, C., *Macromolecules* **1988,** 21 1839-1846.

50. Green, M. M.; Andreola, C.; Munoz, B.; Reidy, M. P.; Zero, K., *J. Am. Chem. Soc.* **1988,** 110, 4063-4065.

51. Schlitzer, D. S.; Novak, B. M., *J. Am. Chem. Soc.* **1998,** 120, (9), 2196-2197.

52. Tian, G.; Lu, Y.; Novak, B. M., *J. Am. Chem. Soc.* **2004,** 126, 4082-4083.

53. Tian, G.; Lu, Y.; Novak, B. M., *Polymer Preprints* **2003,** 44, (2), 693-694.

54. Tang, H.-Z.; Novak, B. M.; He, J.; Polavarapu, P. L., *Angew. Chem. Int. Ed.* **2005,** 44, 7298-7301.

55. Tang, H.-Z.; Lu, Y.; Tian, G.; Capracotta, M. D.; Novak, B. M., *J. Am. Chem. Soc.* **2004,** 126, 3722-3723.

56. Tang, H.-Z.; Boyle, P. D.; Novak, B. M., *J. Am. Chem. Soc.* **2005,** 127, 2136-2142.

57. Bassi, I. W.; Dall'Asta, G.; Campigli, U.; Strepparola, E., *Die Makromolekulare Chemie* **1963,** 60, 213-222.

58. Rosa, C. D.; Corradini, P., *Macromolecules* **1993,** 26, 5711-5718.

59. Lovinger, A. J.; Lotz, B.; Davis, D. D.; F. J. Padden, J., *Macromolecules* **1993,** 26, 3494-3503.

60. Natta, G.; Corradni, P.; Bassi, I. W., *Die Makromolekulare Chemie* **1959,** 33, 247-248.

61. Nishikawa, Y.; Murakami, S.; Kohjiya, S.; Kawaguchi, A., *Macromolecules* **1996,** 29, 5558-5566.

62. Rosa, C. D.; Borriello, A.; Corradini, P., *Macromolecules* **1996,** 29, 6323-6327.

63. Dappen, R.; Arm, H.; Meyer, V. R., *J. Chromatogr* **1986,** 373, 1.

64. Nakano, T.; Okamoto, Y.; Hatada, K., *J. Am. Chem. Soc.* **1992,** 114, 1318-1329.

65. Okamoto, Y.; Honda, S.; Hatada, K.; Okamoto, I.; Toga, Y.; S. Kobayashi, *Bull.Chem. Soc. Jpn.* **1984,** 57, 1681.

66. Okamoto, Y.; Yashima, E.; Hatada, K.; Mislow, K., *J. Org. Chem.* **1984,** 49, 557-558.

67. Okamoto, Y.; Honda, S.; Hatada, K.; Yuki, H., *Bull. Chem, Soc. Jpn.* **1985,** 58, 3053.

68. Okamoto, Y.; Kawashima, M.; Hatada, K., *J. Chromatogr.* **1986,** 373, 173.

69. Okamoto, Y.; Yashima, E.; Ishikura, M.; Hatada, K., *Bull. Chem, Soc. Jpn.* **1988,** 61, 255.

70. Parker, C. E.; Levy, L. A.; Smith, R. W.; Yamaguchi, K.; Gaskell, S. J., *J.Chromatogr* **1985,** 344, 378.

71. Ebrahim, S.; Wills, M., *Tetrahedron: Asymmetry* **1997,** 8, 3163-3173.

72. Pu, L., *Tetrahedron: Asymmetry* **1998,** 9, 1457-1477.

73. Baba, N.; Matsumura, Y.; Sugimoto, T., *Tetrahedron Letters* **1978,** 44, 4281-4284.

74. Ma, L.; Hu, Q.-S.; Musick, K. Y.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L., *Macromolecules* **1996,** 29, 5083 - 5090.

75. Ma, L.; Hu, Q.-S.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L., *Macromolecules* **1997,** 30, 204 - 218.

76. Sugimoto, T.; Matsumura, Y.; Tanimoto, S.; Okano, M., *J. Chem. Soc., Chem. Commun.* **1978**, 926-927.

77. Gamez, P.; Dunjic, B.; Fache, F.; Lemaire, M., *J. Chem. Soc., Chem. Commun.* **1994**, 1417 - 1418.

78. Buckley, G. S.; Roland, C. M., *Polym. Eng. Sci.* **1997,** 37, 138.

79. Pham, V. P.; Manivannan, G.; Lessard, R. A.; Bornengo, G.; Po, R., *Applied Physics Science & Processing* **1995,** A60(3), 239.

80. Ciferri, A., *Ed. Liguid Crystallinity in Polymers*. VCH Publisher, New York: 1991.

81. Lu, Y. Ph.D. Thesis. North Carolina State University, 2005.

82. Ito, Y.; Ihara, E.; Murakami, M., *Angew. Chem. Int. Ed. Engl.* **1992,** 31, 1509-1510.

83. Ito, Y.; Miyake, T.; Ohara, T.; Suginome, M., *Macromolecules* **1998,** 31, 1697-1699.

84. Hoshikawa, N.; Hotta, Y.; Okamoto, Y., *J. Am. Chem. Soc.* **2003,** 125, (41), 12380 - 12381.

85. Lim, A. R.; Novak, B. M., *Solid State Communications* **1999,** 112, 459–464.

86. Blackburn, J. L. Ph.D. Thesis. North Carolina State University, 2004.

87. Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W., *J. Am. Chem. Soc.* **1988,** 110, 6818-6825.

88. Goodwin, A.; Novak, B. M., *Macromolecules* **1994,** 27, 5520-5522.

89. Keck, G. E.; Krishnamurthy, D., *J. Am. Chem. Soc.* **1995,** 117, 2363-2364.

90. Terada, M.; Matsumoto, Y.; Nakamura, Y.; Mikami, K., *Inorg. Chim. Acta.* **1999,** 296, 267.

91. Yuki, H.; Hatada, K.; Kikuchi, Y.; Niinomi, T., *J. Polym. Sci. Part B* **1968,** 6, 753.

92. Yuki, H.; Hatada, K.; Kikuchi, Y.; Niinomi, T., *Polym. J.* **1970,** 1, 36.

93. Nakano, T.; Okamoto, Y., *Macromolecules* **1999,** 32 2391-2393.

94. Nakano, T.; Mod, M.; Okamoto, Y., *Macromolecules* **1993,** 26 861-860.

95. Verbit, L.; Halbert, T. R.; Patterson, R. B., *J. Org. Chem.* **1975,** 40, 1649-1650.

96. Saeva, F. D.; Sharpe, P. E.; Olin, G. R., *J. Am. Chem. Soc.* **1975,** 97, 204-205.

Chapter II.

Asymmetric Cationic Polymerization initiated by Cationic Zirconocene Complexes possessing Chiral Counter Anions

2.1. Introduction

We are interested in controlling the stereoregularity of synthetic vinyl polymers and generating single handed helical polymers. Several factors can influence stereoregularity including the ligands on the catalyst, temperature, pressure, and solvents. In ionic systems there is also the possibility of having counterion effects. In this study, we are interested in the effects of counterions in cationic polymerizations. Our research focuses on using cationic zirconocene complexes possessing chiral counteranions to initiate and control asymmetric cationic polymerizations.

Asymmetric induction is an extremely sensitive phenomenon, with high enantioselectivities requiring only very small differences in transition state energies.[1] It has recently been demonstrated that ionic interactions in metal catalysis are not only important but can be utilized to influence chirality in reaction products.[1-4] Ionic interactions also can be expected to influence stereoregular polymerizations. The concept of asymmetric polymerizations using chiral counter ions has been studied in helix sense selective anionic polymerization using lithium counter cations with chiral chelating ligands and the methacylates with bulky ester groups. The resulting polymers (e.g., poly(triphenylmethyl methacrylate)) have a high helix-sense excess and the high optical activity since the chiral counter cations at the propagating sites create a chiral reaction environment.[2,3]

If cationic zirconocene complexes possessing chiral counterions are used (Figure 2.1), is it possible that they can initiate and polymerize monomers for cationic polymerization and can control the stereoregularity and helix sense selectivity of the polymers?

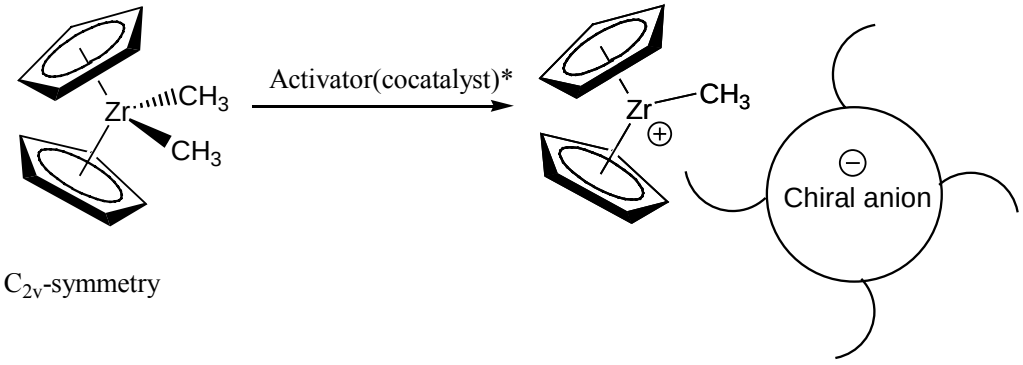


Figure 2.1. C_{2v}-symmetric organometallic complex possessing a chiral counter anion.

Both configurational tacticity and conformational atropisomerism control are needed for asymmetric cationic polymerization. The configuration of polymers can be controlled by both initiators and monomers. Asymmetric cationic polymerization requires appropriate initiators and monomers that will control the stereoregularity of the chains to yield highly isotactic or syndiotactic polymers, since these stereoregular polymers can adopt helical conformations. Initiators should possess chirality to select for a preferred helical conformation. Once a preferred helical conformation is induced by chiral inititators, the side group must be large enough to prevent racemization through main-chain bond rotations.

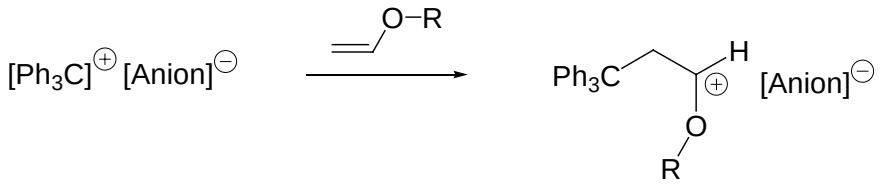
In order to reach the goal of this research, the cationic zirconocene complex with racemic counter anions should polymerize bulky vinyl ether monomers through a cationic polymerization, the resulting polymers should be stereoregular polymers. To carry out helix-sense selective polymerizations, cationic zirconocene complexes with chiral counter anions need to be synthesized.

Generally strong acids with non-nucleophilic counter anions are used to initiate this polymerization. If the anions have nucleophilicity, they induce termination and chain transfer.[5,6] Vinyl ethers are an important monomer class for cationic polymerization since they have a strongly electron-donating alkoxy substituent which helps to stabilize the propagating carbocation. The initiation step is the electrophilic attack of a cation on the vinyl ether double bond and the propagation step involves successive additions of monomers to the propagating carbocation (Figure 2.2). The counter anions always exist around the propagating site. In order to get high molecular weight polymers, non polar solvents or low temperatures are generally used since the instability of the propagating carbocation tends to transfer its β proton either to the counter anion or to incoming monomers.[7,8]

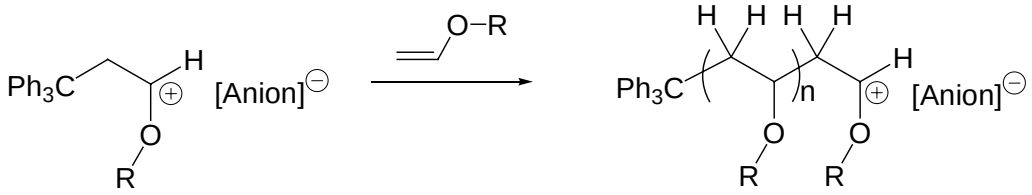
In our study, it will be important to choose the appropriate chiral counter anion for successful asymmetric cationic polymerizations. The chiral counter anion should have both configurational and chemical stability, should be a non-coordinating and non-nucleophilic anion, and should be easily separable from the reaction medium.

Configurationally stable TRISPHAT anion, which was shown to be readily synthesized and resolved,[9] is our candidate chiral anion (Figure 2.3). It has recently been reported that chiral TRISPHAT anions can be used as efficient NMR chiral shift reagents and

Initiation:



Propagation:



Chain transfer:

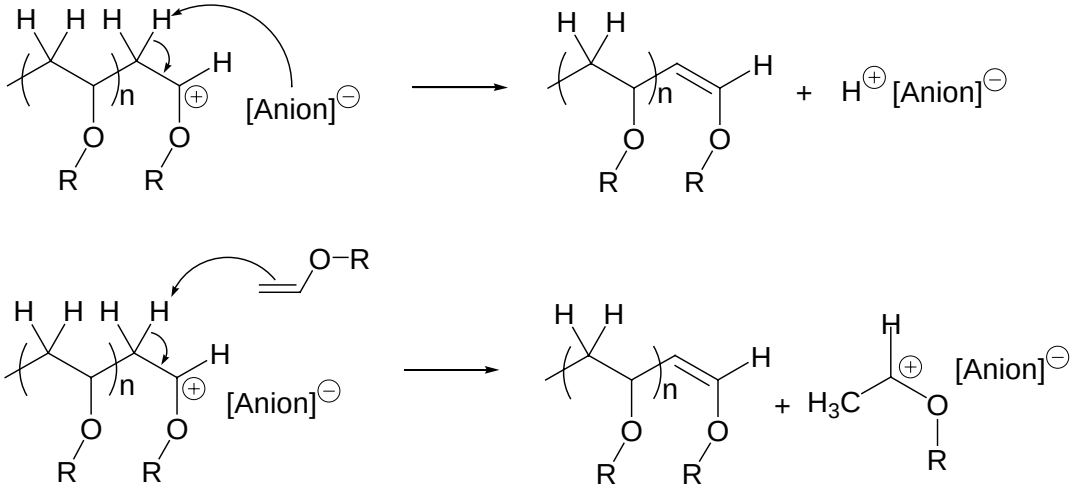


Figure 2.2. The general mechanism of cationic polymerization of vinyl ether monomers.

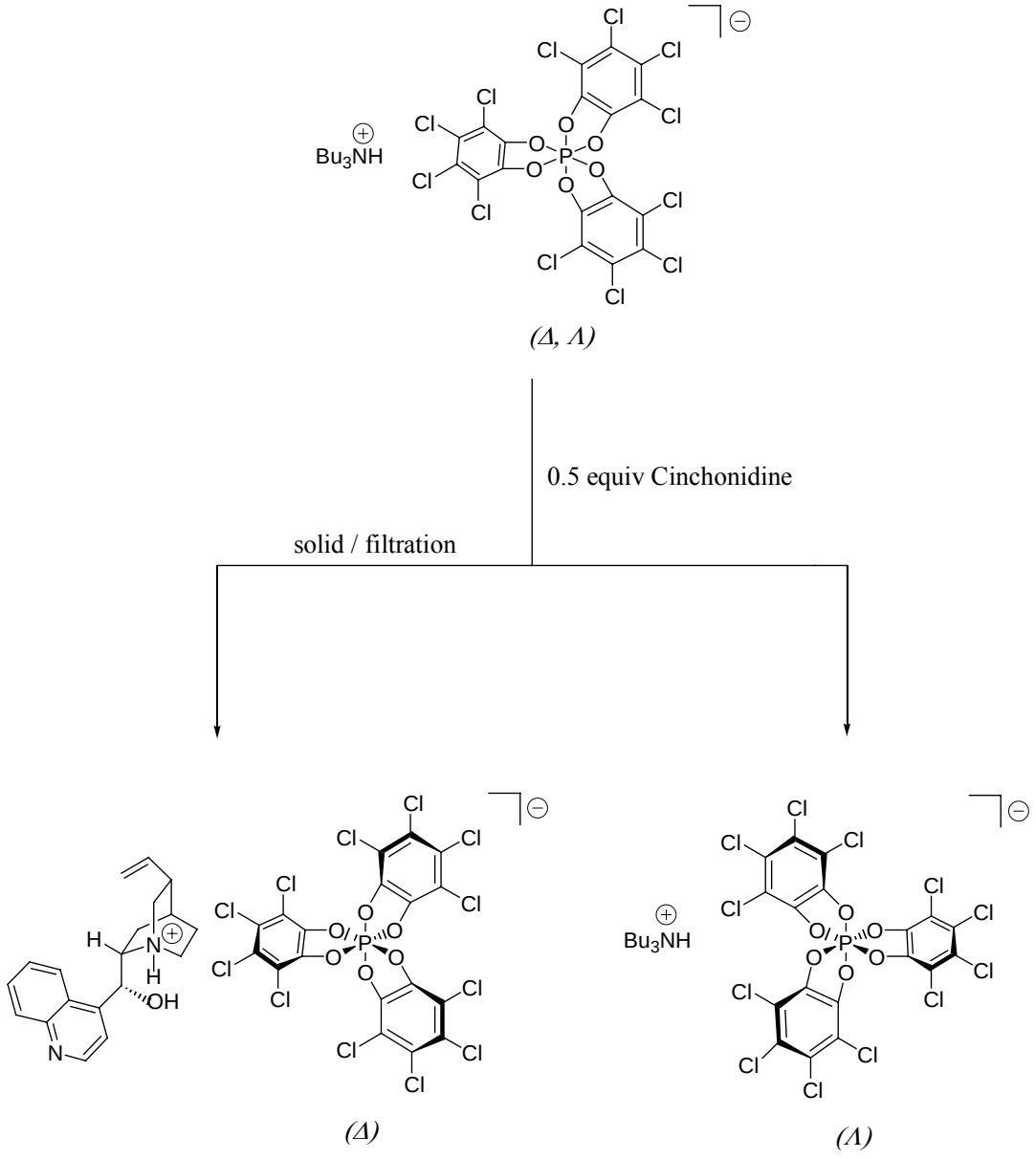


Figure 2.3. Resolution of a chiral TRISPHAT anion.

used to induce strong optical activity in configurationally unstable racemic cations, determine enantiomeric purities, and resolve chiral cationic complexes.[10-12] For instance, it was recently shown that these chiral anions were effective at introducing asymmetry into $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline). When associated with the labile cation, in solution, TRISPHAT controls its configuration with high diastereoselectivity (d.r. > 49:1 in $CDCl_3$ in favor of $[\Delta\text{-}Fe(phen)_3][\Delta\text{-}TRISPHAT]_2$).[13]

We need to pair appropriate activators with TRISPHAT anions in order to synthesize the cationic zirconocene salts. There are several cocatalysts such as MAO, trityl and ammonium borate and aluminate salts which activate zirconocene compounds, are converted to anions, and lead to a catalytically active cation-anion ion pair.[14]

Many kinds of highly efficient activators have been developed. The trityl cation Ph_3C^+ is a powerful alkide-abstracting reagent, and ammonium cations $HNRR'_2^+$ can readily cleave metal alkyl bonds via protonolysis. In combination with non-coordinating/weakly coordinating anions, several activators such as $[Ph_3C][B(C_6F_5)_4]$,[15,16] $[Ph_3C][Al(C_6F_5)_4]$,[17] and $[HNRR'_2][B(C_6F_5)_4]$,[18-20] have been developed as effective cocatalysts for activating metal alkyls, thereby yielding highly efficient olefin polymerization catalysts.

We are interested in trityl cocatalysts since after activation byproducts, Ph_3CCH_3, could not terminate or chain-transfer the propagating sites for cationic polymerization. Generally trityl cocatalysts are prepared by ion exchange metathesis with triphenylmethyl chloride Ph_3CCl and lithium salts possessing non-coordinating/weakly coordinating anions.[14,15,21,22] Here is an example of the synthesis of a trityl cocatalyst and the activation process of a zirconocene compound. Rausch and coworkers synthesized triphenylcarbenium

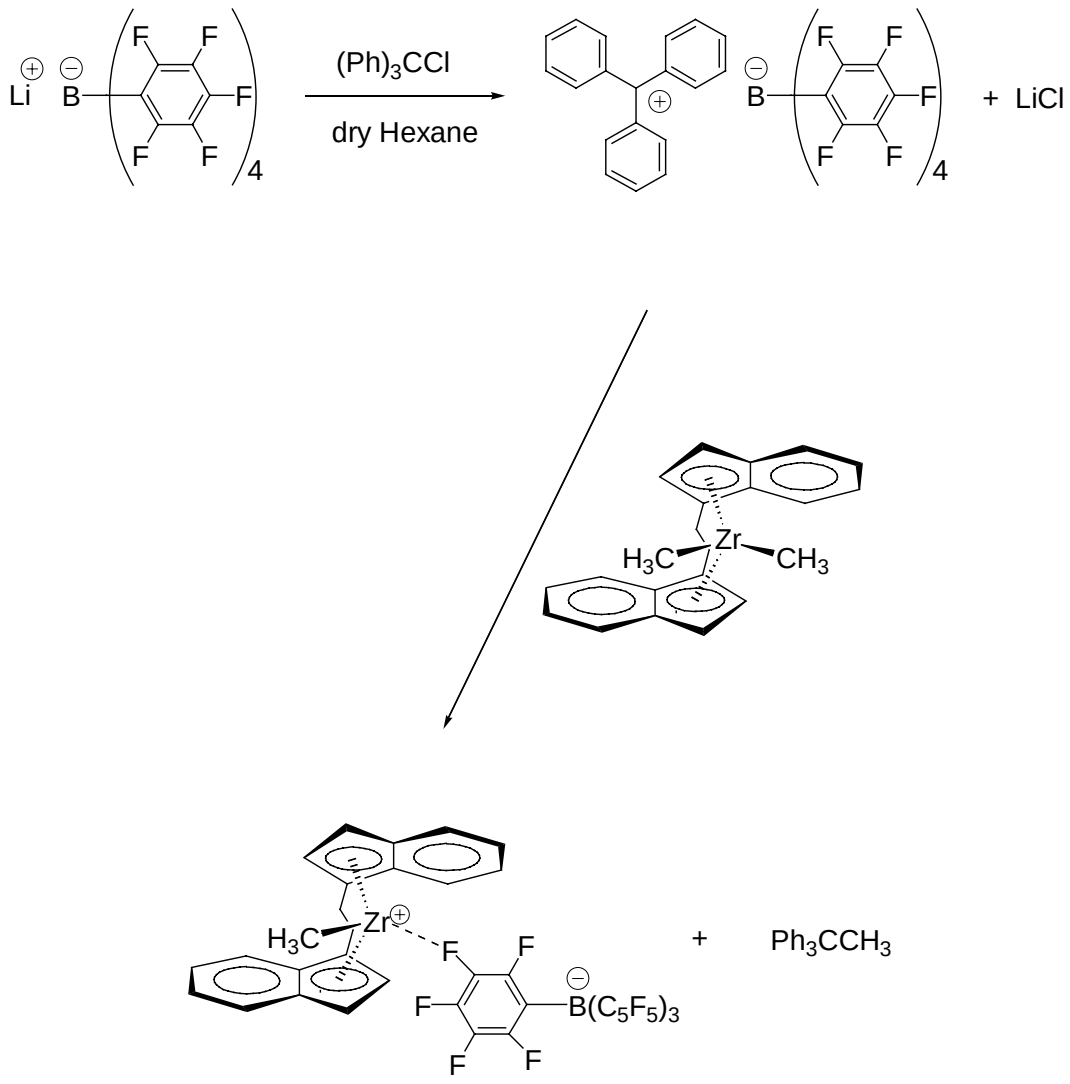


Figure 2.4. The systhesis of cocatalysts and cationic zirconium complexes after activation process.

tetrakis(pentafluorophenyl)borate by mixing lithium tetrakis(pentafluorophenyl)borate and triphenylmethyl chloride. The cationic zirconium complex $[Et(Ind)_2ZrMe][B(C_6F_5)_4]$ was then synthesized by the reaction of neutral zirconium complex, $Et(Ind)_2ZrMe_2$, and the trityl cocatalysts (Figure 2.4).[15]

A wide range of single site organometallic catalysts have been developed for the coordination insertion polymerization of simple olefins.[23-27] Likewise, utilization of a Lewis acid, particularly with early transition-metal complexes, to promote carbocationic polymerization of vinyl ethers also has been reported.[28-32]

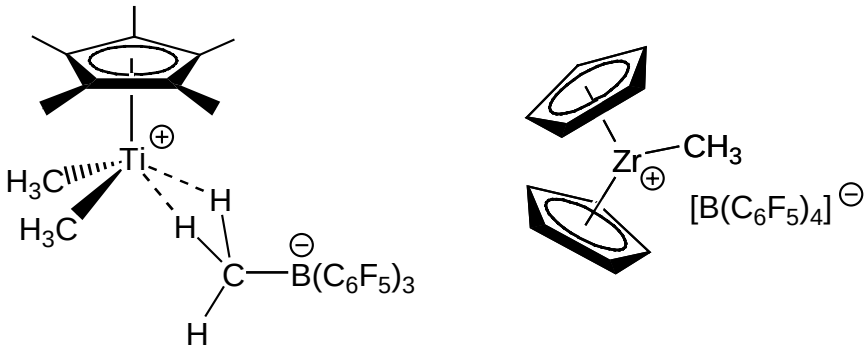
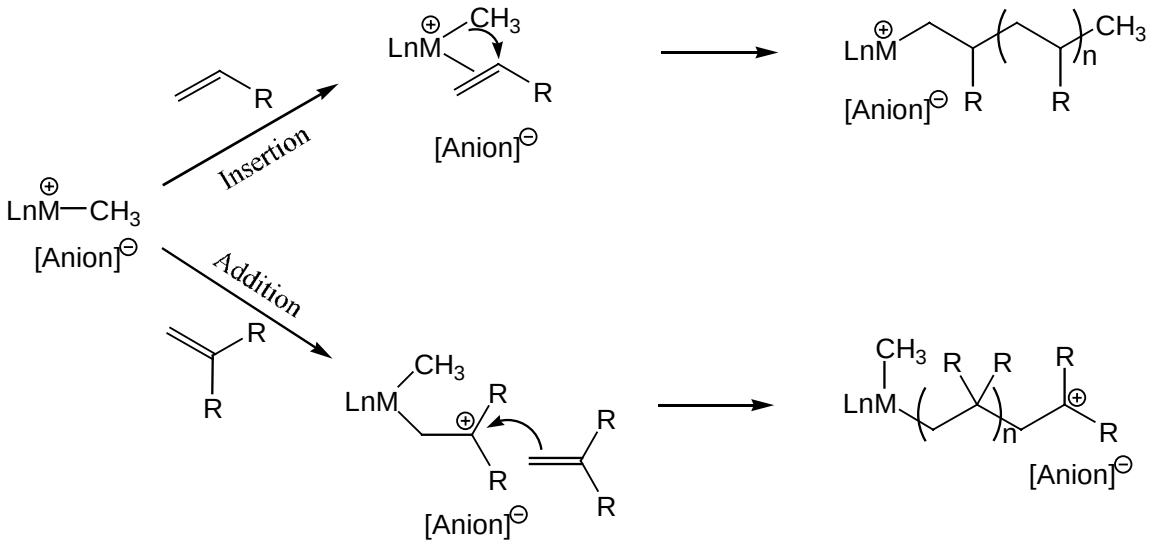


Figure 2.5. Cationic titanium and zirconocene initiators for cationic polymerization.

Since cationic early transition metal species such as $[Cp_2ZrMe]^+$ and $[(\eta_5\text{-}C_5Me_5)TiMe_2]^+$ are very strong electrophiles, in combination with monomers that can generate carbocations such as styrene, isobutene, vinyl ethers, and N-vinylcarbazole, they can be used to initiate cationic polymerization (Figure 2.5).[29-31] According to Mark's group, $[(\eta^5\text{-}C_5Me_5)TiMe_2][CH_3B(C_6F_5)_3]$ polymerizes vinyl ethers through a cationic polymerization and the polymers generally exhibit unusually high molecular weights and

narrow molecular weight distributions.[31] The polyvinylethers are formed via carbocationic initiation by the titanium-containing cationic complex $[(\eta_5\text{-}C_5Me_5)TiMe_2]^+$ rather than via Ziegler-Natta processes.[30,31]



Sheme 2.1. Two polymerization pathways of cationic early transition metal species.

Generally the catalyst systems such as $[Cp_2ZrMe][B(C_6F_5)_4]$ polymerize olefins by a Ziegler-type coordination-insertion mechanism. Since cationic species such as $[Cp_2ZrMe]^+$ are very strong electrophiles, an alternative polymerization pathway could be expected whereby the addition of an olefin to $[Cp_2ZrMe]^+$ leads not to insertion into the M–C bond but to the formation of a carbocation (scheme 2.1). Bochamann's group have reported $[Cp_2ZrMe]^+$ initiators can be used as initiators for carbocationic isobutene homo- and copolymerizations.[33] The polyisobutenes are formed via carbocationic initiation by the cationic zirconocene complex $[Cp_2ZrMe]^+$ rather than via Ziegler-Natta processes.[28,33-35]

The highly electrophilic nature of $[Cp_2ZrMe]^+$ cations can be employed to develop novel initiator systems for the carbocationic polymerization of vinyl ethers.

For helix sense selective cationic polymerization bulky vinyl ethers are required since bulky side group can lead to high helix inversion barriers and prevent racemization through main-chain bond rotations. It is well known that vinyl ethers such as *tert*-butyl vinyl ether (*t*BVE) has been studied as a starting monomer to obtain stereoregular poly(vinyl alcohol) since bulky side chains can induce stereoregular polymers.[36-40] Some modified Friedel-Crafts catalysts were studied in the cationic polymerization of the tert-buty1 vinyl ether in the homogeneous phase.[38] The highest stereospecificity of the polymer is obtained in the case of boron containing compounds, such as boron monoalkyl difluorides or boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$).[39-42]

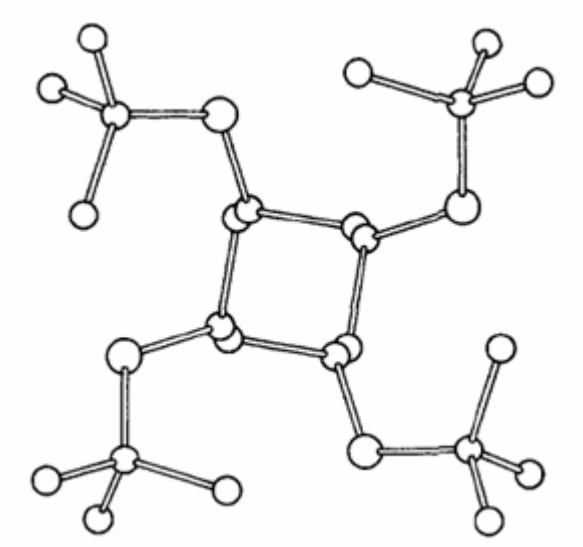


Figure 2.6. Projection of the chain of isotactic poly *tert*-butyl vinyl ether on (001) plane.[39]

According to the X-ray studies of oriented fibers of the isotactic poly *t*-butyl vinyl ethers, the polymer chains have a four-fold helical conformation and are a racemic mixture in the solid state (Figure 2.6).[39] Because of its known high tacticity, *tert*-butyl vinyl ether will be our starting monomer for this research.

This research focuses on using cationic zirconocene complexes possessing chiral counteranions to initiate and polymerize bulky vinyl ether monomers and to control stereoregularity of the polymers and asymmetric carbocationic polymerizations.

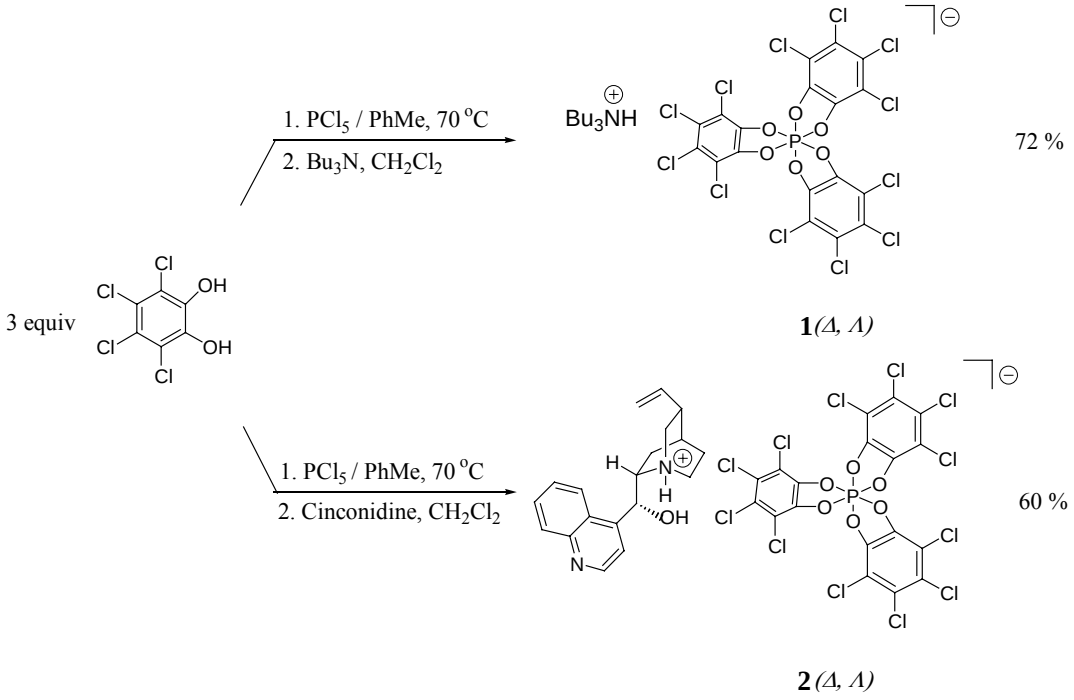
2.2. Results and Discussion

2.2.1. The synthesis of triphenylcarbenium *rac*-tris(tetra-chlorobenzenediolato) phosphate, 4

We need appropriate activators with *rac*-TRISPHAT anions to synthesize cationic zirconocene complexes. We will synthesize and use the triphenylcarbenium *rac*-TRISPHAT salt for activating zirconocene compounds since the trityl cation is a powerful alkide and hydride-abstracting reagent. In combination with non-coordinating/weakly coordinating anions, trityl cation has been developed as an effective cocatalyst for activating metallocene compounds.[14-16]

Trityl *rac*-TRISPHAT, **4**, was prepared by using ion exchange methods, which have been previously developed to synthesize trityl cation with other non-coordinating/weakly coordinating anions.[15,16]

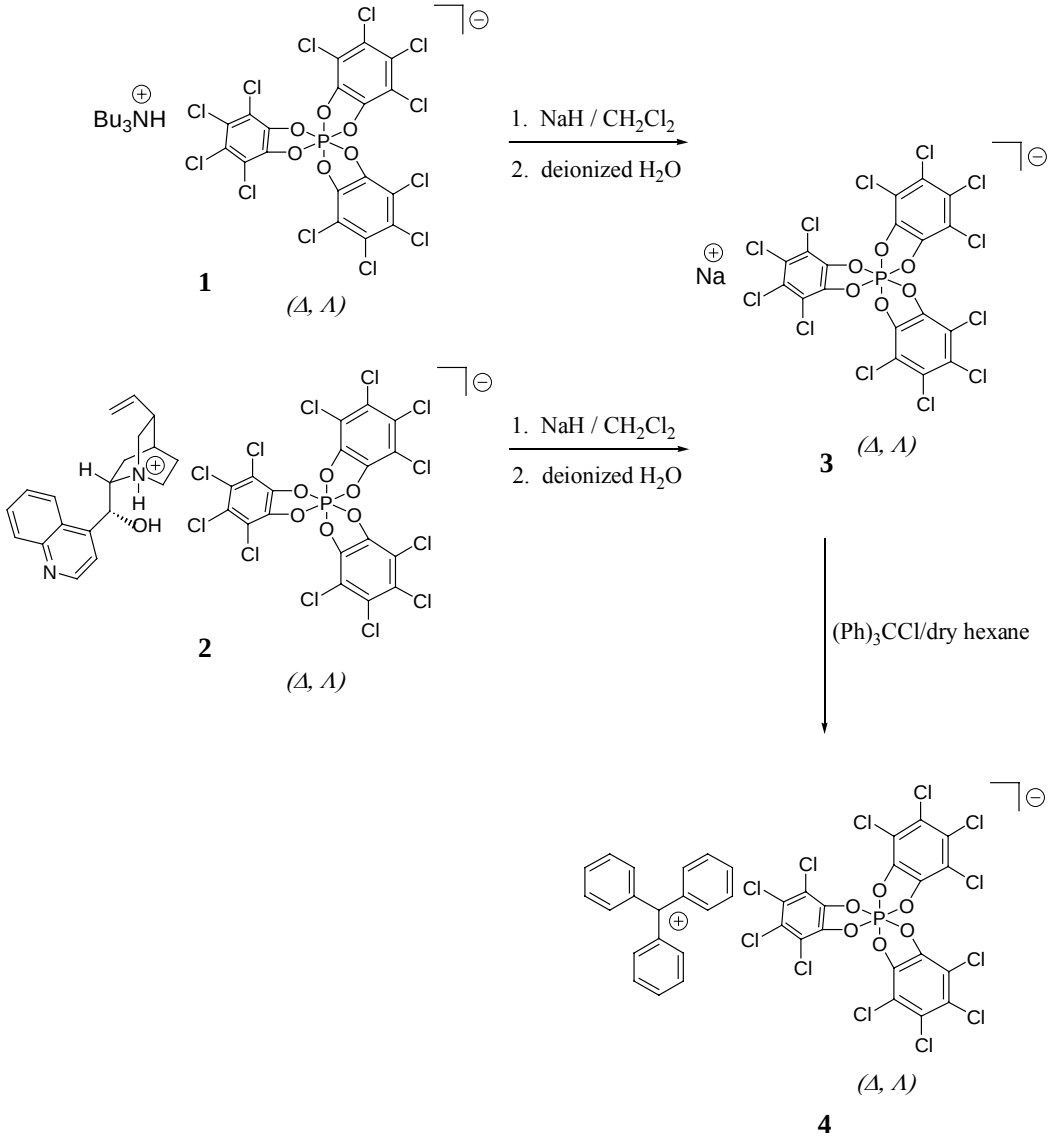
According to published procedures,[9] tributylammomium *rac*-TRISPHAT **1** (72%) and cinchonidium *rac*-TRISPHAT **2** (60%) were prepared since these two salts can be resolved as ammonum salts with chiral anions (Scheme 2.2).[12]



Scheme 2.2. The synthesis of tributylammomium and cinchonidium *rac*-TRISPHAT.

First we needed sodium *rac*-TRISPHAT salt **3** to synthesize triphenylcarbenium *rac*-tris(tetra-chlorobenzenediolato)phosphate **4** via a direct ion exchange method. The reaction of tributylammomium *rac*-TRISPHAT **1** with sodium hydride leads to sodium *rac*-TRISPHAT **3** (98 %), which results from ion exchange by the strong base (Scheme 2.3).

Using the same method, sodium *rac*-TRISPHAT salt **3** (97%) was also prepared from cinchonidium *rac*-TRISPHAT salt **2** (Scheme 2.3). The sodium *rac*-TRISPHAT salt **4** was characterized by ^{31}P NMR spectroscopy since the ^{31}P NMR spectra of *rac*-TRISPHAT anions show a single signal in the region from δ = - 79 to – 82.[10-12]



Scheme 2.3. The synthesis of triphenylcarbenium *rac*-TRISPHAT.

We then used ion exchange metathesis to synthesize triphenylcarbenium *rac*-tris(tetra-chlorobenzenediolato)phosphate, **4**. Ion exchange metathesis with sodium *rac*-TRISPAT salt **3** and triphenylmethyl chloride (Scheme 2.3) yielded the corresponding triphenylcarbenium *rac*-tris(tetra-chlorobenzenediolato)phosphate **4** (85.7%), which was characterized by standard spectroscopic techniques, as well as by single-crystal X-ray diffraction.

2.2.2. Results of single crystal X-ray diffraction of trityl *rac*-TRISPHAT salt, 4

We have synthesized trityl *rac*-TRISPHAT salts, **4,** as a new cocatalyst for activating zirconocene compounds. The trityl cation is chiral when the three phenyl rings are not mutually coplanar, forming propeller shaped Δ and Λ enantiomers. In solution, the two enatiomers racemize rapidly, while in the solid state the configurations are typically fixed by crystal packing forces.[43,44]

The chiral and configurationally stable tris(tetrachlorobenzenediolato)phosphate(V) (TRISPHAT) anion has been recently reported as an efficient NMR chiral shift reagent and can used to induce strong optical activity in configurationally unstable racemic cations and resolve chiral cationic complexes.[10-12].

We have prepared the trityl *rac*-TRISPHAT salts, **4,** in the attempt to induce an enantionmerically pure and configurationally stable form of the trityl cation to crystallize. The salt was characterized by a number of techniques including single crystal X-ray crystallography.

The trityl *rac*-TRISPHAT compound, **4**, crystallizes with four molecules in the asymmetric unit ($Z' = 4$). All moieties reside at general positions in the unit cell. The four

cations are labeled a, b, c, and d, while the four anions are labeled e, f, g, and h. The numbering of the atoms is identical for cations and anions respectively. The geometries of the symmetry independent cations are similar and a representative molecular plot is given in Figure 2.7. Similarly, the four symmetry independent anions have similar molecular geometries and a representative plot of one of the anions is given in Figure 2.8.

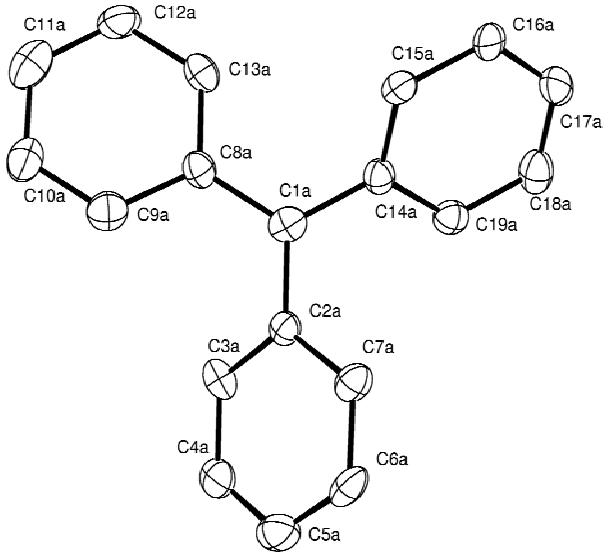


Figure 2.7. The ORTEP diagram of the trityl a (Δ) cation.

Most bond distances within all the cations agree well with previously published results for the trityl cation.[43] The aromatic rings of the a(Δ) cation show no significant deviations from planarity and C1a lays within one standard uncertainty unit of the C2a-C8a-C14a plane. The dihedral angles between the planes of the aromatic rings and the C2a-C8a-C14a plane are

38.8(2), 16.1(2), and 40.6(2). The other trityl cations, b(*Λ*), c(*Δ*), and d(*Λ*), all have similar values.

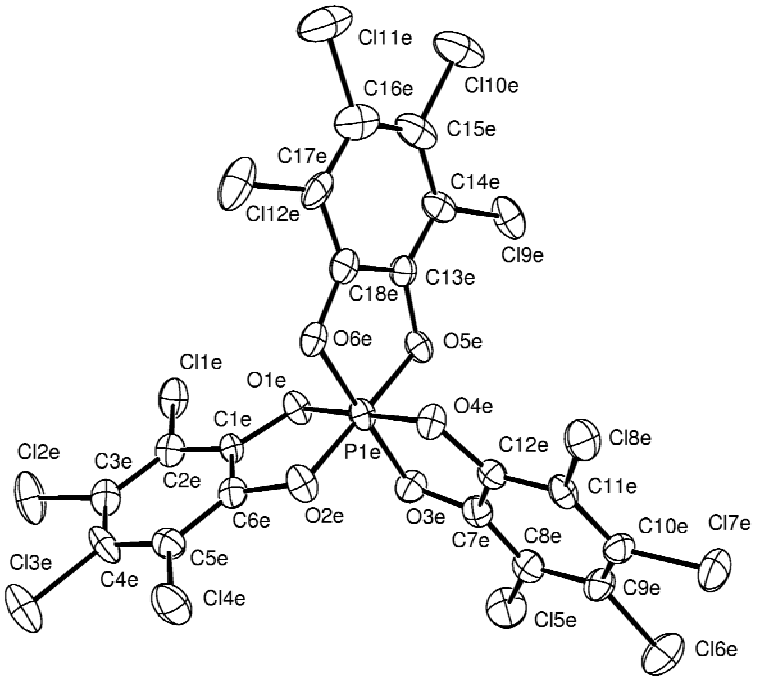


Figure 2.8. The ORTEP diagram of the TRISPHAT e (*Δ*) anion.

Most bond distances within all the anions agree well with previously published results for the TRISPHAT anion.[9,45] The average P-O bond lengths in anions, e, f, g, h are 1.718 Å, 1.714 Å, 1.715 Å, and 1.719 Å. The chelate rings of the e(*Δ*) anion show no significant deviations from planarity. The dihedral angles between the planes of the chelate rings and the O1e-O2e-O6e plane are 57.09(14), 57.23(14), and 52.28(15). The other TRISPHAT anions, f(*Δ*), g(*Λ*), and h(*Δ*), all have similar values.

The most notable feature of the crystal structure is the observation that while the absolute configuration of the cations in the asymmetric unit are equally distributed between *Δ* and *Λ*, as *Δ, Λ, Δ, Λ* for a, b, c, and d respectively, the anions in the asymmetric unit are unequal in their distribution of optical isomers. The anionic optical isomeric distribution is *Δ, Δ, Λ, Δ* for e, f, g, h respectively. This is in contrast to another TRISPHAT-carbenium structure, tris(4-dimethylaminobenzene)carbenium TRISPHAT[46] in which there was an equal distribution of optical isomers for both cations and anions.

2.2.3. Polymerization of tert-butyl vinyl ether

Tert-butyl vinyl ether has been studied as a monomer to obtain stereoregular poly(vinyl alcohol) since the steric structure of the vinyl ether can induce stereoregular polymers in cationic polymerization.[36-40] We therefore used this monomer as a starting point with three different cationic initiation systems for polymerization (Scheme 2.4).

First, for a homogeneous cationic polymerization, we used the trityl *rac*-TRISPHAT, **4.** solution with CH_2Cl_2/toluene solvent (5:1) since the initiator had low solubility in toluene. The polymerizations of *t*-butyl vinyl ether, initiated by trityl *rac*-TRISPHAT, **4**, was very rapid in this solvent at -78ºC and results in sticky oils which were characterized as poly(*t*-butyl vinyl ether) by ^{1}H NMR spectroscopy (Figure 2.9).[40]

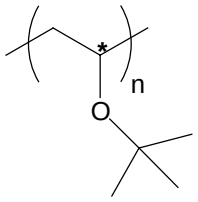
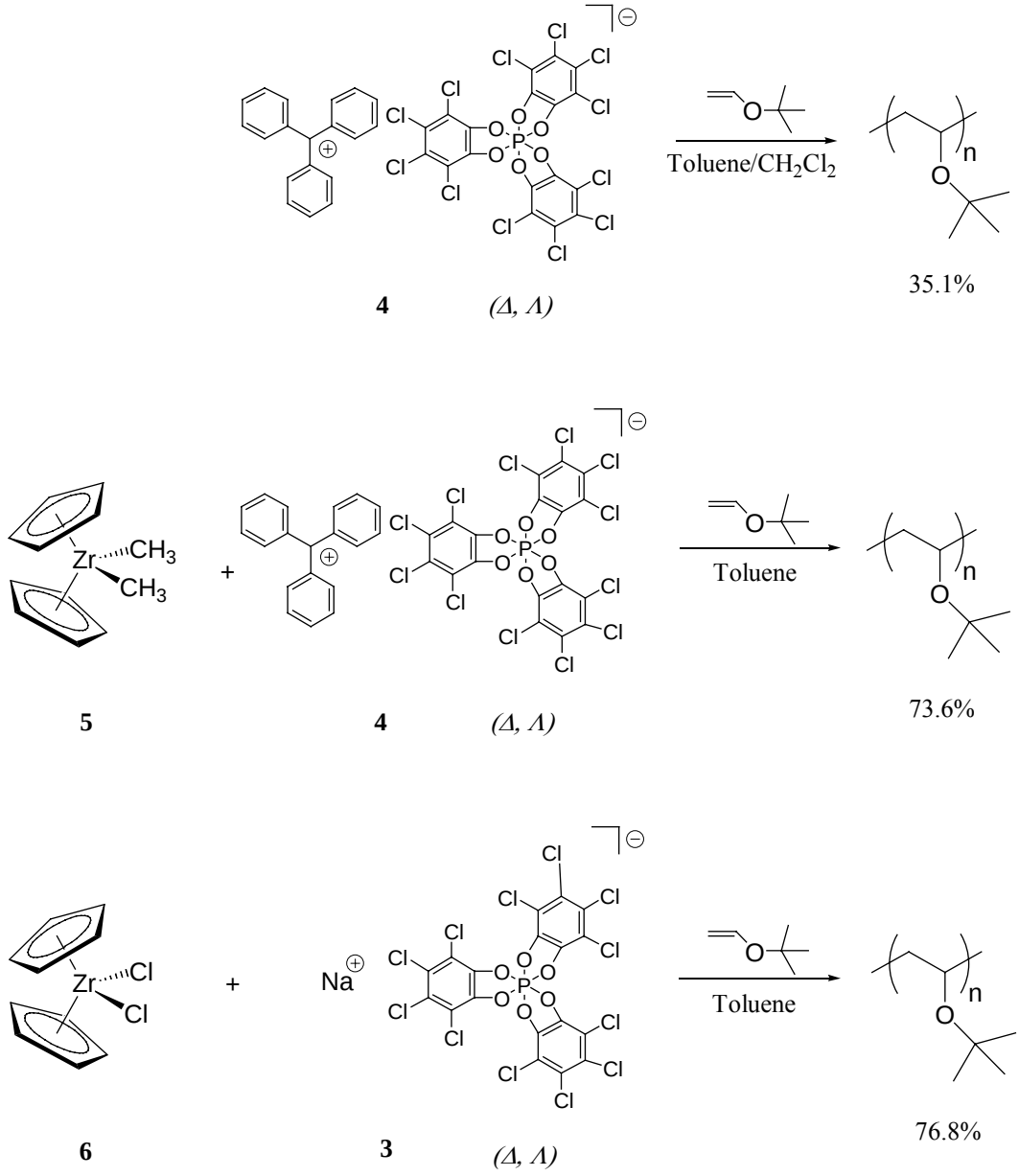


Figure 2.9. Poly (*t*-butyl vinyl ether).



Scheme 2.4. The cationic polymerizations of *t*-butyl vinyl ether.

Analysis of the β-methylene (the asterisked carbon in Figure 2.9) resonance[40] in the $^{13}C\{^{1}H\}$ NMR spectrum can be used to determine the tacticity of the polymer. This analysis indicated the formation of an atactic polymer (58% r dyads, 42% m dyads: 34% rr triads, 48% mr triads, 18% mm triads).

Second, the polymerization of *t*-butyl vinyl ether, initiated by trityl *rac*-TRISPHAT, **4,** and bis(cyclopentadienyl)dimethylzirconium, **5**, was very rapid in toluene at -55ºC and results in sticky oils which were also characterized as poly(*t*-butyl vinyl ether) by ^{1}H NMR spectroscopy.[40] No polymerization occurred below -55ºC. Analysis of β-methylene (the asterisked carbon in Figure 2.9) resonance[40] in the $^{13}C\{^{1}H\}$ NMR spectrum indicated the formation of an atactic polymer (53% r dyads, 47% m dyads: 28% rr triads, 50% mr triads, 22% mm triads).

Table 2.1. Polymerizations of *tert*-butyl vinyl ether.[a,b]

						triads obsd(%)			diads calcd(%)	
initiator	solvent	temp(°C)	yield(%)	Mw(10^{-4})	Mw/Mn	mm	mr	rr	m	r
4	toluene/CH_2Cl_2(5:1)	-78	35.1	0.97	1.6	18	48	34	42	58
4 + **5**	toluene	-55	73.6	1.16	1.5	22	50	28	47	53
3 + **6**	toluene	-50	76.8	1.76	1.7	24	48	28	48	52

[a]Monomer/Initiator = 500, all concentrations of **3**, **4**, **5**, **6** are 0.01 M, monomer = 2 mL (15 mmol)respectively, solvent = 3 mL, polymerization time = 3 mins. [b]Diad values were calculated by means of the following equations: (m) = (mm) + ½(mr); (r) = (rr) + ½(mr).

The polymerization of *t*-butyl vinyl ether, initiated by sodium *rac*-TRISPHAT, **3,** and bis(cyclopentadienyl)zirconiumdichloride, **6**, was very rapid in toluene at -50ºC and results in sticky oils which were characterized as poly(*t*-butyl vinyl ether) by ^{1}H NMR spectroscopy.[40] No polymerization occurred below -50ºC. Analysis of β-methylene (the asterisked carbon in Figure 4) resonances[40] in the $^{13}C\{^{1}H\}$ NMR spectrum indicated the formation of an atactic polymer (52% r dyads, 48% m dyads: 28% rr triads, 48% mr triads, 24% mm triads).

Using three different cationic initiation systems, the *tert*-butyl vinyl ether was polymerized. The polymers were obtained in reasonable yields, and showed reasonable molecular weights and molecular weight distributions. Unfortunately, these three systems did not control the stereoregularity of the polymers, as they all produced atactic materials (Table 2.1).

2.3. Conclusions

New cocatalysts, Sodium *rac*-tris(tetra-chlorobenzenediolato)phosphate, **3,** and triphenylcarbenium *rac*-tris(tetra-chlorobenzenediolato)phosphate, **4,** for cationic ziconocene complexes were synthesized**,** respectively. The X-ray single crystal structure of **4** showed that the crystal structure contains a racemic mixture and there are four ion pairs in the asymmetric unit and eight ion pairs in the unit cell. The most interesting part is that the distribution of *Δ*-isomers and *Λ*-isomers is equal in the unit cell, but the anionic isomers in the asymmetric unit are predominantly (75%) one isomer. Poly (*tert*-butyl vinyl ether) samples were synthesized by the initiating system of bis (cyclopentadienyl)dimethylzirconium, **5,** and trityl *rac*-TRISPHAT, **4,** and by the initiating system of sodium *rac*-TRISPHAT, **3,** and bis (cyclopentadienyl)zirconiumdichloride, **6**. The

polymers exhibited reasonable yields**,** reasonable molecular weights, and reasonable molecular weight distributions, respectively. Unfortunately, these systems did not control the stereoregularity of the polymers.

2.4. Experimental section

General procedures and characterizations

All synthetic manipulations were conducted in either a MBraun UNILab drybox under nitrogen atmosphrere or using a Schlenk line under an inert atmosphere of nitrogen. Dry and degassed solvents (MBraun solvent system) were used throughout.

^{1}H NMR spectra were obtained at 300 MHz and 400 MHz with Varian-Mercury NMR spectrometers. Chemical shifts for ^{1}H NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane and are referenced to selected residual proton peaks of the solvent as follows: $CDCl_3$, 7.27, singlet; Acetone-d_6, 2.05 quintet. Significant ^{1}H NMR data are tabulated in order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constant in Hertz, number of protons. $^{13}C\{^{1}H\}$ NMR proton decoupled NMR spectra were measured at 100 MHz on a Varian-Mercury spectrometer. Chemical shifts for $^{13}C\{^{1}H\}$ NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to selected residual peaks of the solvents as follows: $CDCl_3$, CD_2Cl_2. CD_2Cl_2 was stirred over CaH_2 overnight before being distillated and degassed. ^{31}P NMR spectra were measured at 162 MHz on a Varian-Mercury spectrometer. Chemical shifts for ^{31}P NMR spectra are reported in δ (ppm) and are referenced to a selected residual peak of the Cinchonidium *rac*-TRISPHAT in acetone-d_6 solvent.

Before sample analysis, solvents were removed with a rotary evaporator and under Schlenk line vacuum (approximately 60 mTorr). Toluene, methylene dichloride, and hexane used for polymerization reactions and reactions with air and moisture sensitive materials were purified by passing through one column filled with activated A2 Alumina catalyst and one column filled with activated Q5 copper catalyst under nitrogen atmosphere (MBraun solvent system). The monomers, t-butyl vinyl ether (99%) were obtained from Aldrich and stirred over CaH_2 overnight before being distillated and degassed. Unless indicated, all materials were purchased from Aldrich Chemical Company or Strem Inc.

Experimental procedures and characterizations

Tri-*n*-butylammonium *rac*-tris(tetra-chlorobenzenediolato)phosphate, 1.

Tributylammomium TRISPHAT was prepared as previously reported[9]. In a three-necked 250 mL round-bottomed flask equipped with a septum, a condenser connected via a tap to a double-manifold gas/vacuum Schlenk line, and a magnetic stirring bar was introduced 3.9 g of PCl_5 (18.7 mmol). The reaction was placed under inert atmosphere (N_2) and dry toluene (60 mL) was added via a cannula. The resulting suspension was heated at 50 °C to give a yellowish colored solution. The tap on the top of the condenser was replaced by a gas trap filled with concentrated aqueous NaOH. Under a strong flow of dinitrogen, tetrachlorocatechol (15.21 g, 61.4 mmol) was slowly added in the solution at 50 °C. During the addition, a precipitate appeared and the suspension turned green. The reaction was then stirred at 70 °C for 24 h. It was then allowed to cool to room temperature, and the toluene was removed slowly under reduced pressure. The resulting light-brown solid was dried under high vacuum for 24 h. Then, at room temperature, dry CH_2Cl_2 (70 mL) and *n*-hexane

(5 mL) were added. The suspension was stirred for 15 min and then nBu$_3$N (4.76 mL, 19.9 mmol) was added in the solution and the reaction was stirred at room temperature for 24 h. The crude solid was filtered over a Büchner funnel. Recrystallization from CH_2Cl_2 gave white crystal to afford chemically pure salt [nBu$_3$NH][*rac*-TRISPHAT] (12.87 g, 13.46 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (br,s, 1H), 3.03 (m, 6H), 1.61 (m, 6H), 1.34 (m, 6H), 0.93 (t, 9H); ^{31}P NMR (162 MHz, CDCl3) δ -79.8.

Cinchonidium *rac*-tris(tetra-chlorobenzenediolato)phosphate, 2.

Using the same method, cinchonidium TRISPHAT salt 2 (60%) was also prepared. ^{31}P NMR(162 MHz, acetone-d_6) δ -79.4; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.91 (d, 1H), 8.21 (d, 1H), 8.09 (d, 1H), 7.79 (d, 1H), 7.75 (dd, 1H), 7.58 (dd, 1H), 6.29 (br, 1H), 5.83 (ddd, 1H), 5.06 (2d, 2H), 6.31 (dd, 1H), 4.47 (ddd, 1H), 4.12 (dddd, 1H), 3.93 (dd, 1H), 3.63 (dd, 1H), 3.62 (dddd, 1H), 3.3-2.5 (br, 2H, OH and NH+), 2.38 (dd, 1H), 2.31 (ddd, 1H), 2.23 (dd, 1H), 2.10 (dddd, 1H), 1.84 (dddd, 1H).

Sodium *rac*-TRISPHAT, 3, from tributylammomium *rac*-TRISPHAT, 1, and cinchonidium *rac*-TRISPHAT salt, 2 .

Sodium hydride 1.5 equivalents was added to tributylammomium *rac*-TRISPHAT salt (1.00 g, 1 mmol) in 100 mL of CH_2Cl_2. The mixture was then stirred for 12 h at room temperature during which time a white solid precipitated. Deionized water (100 mL) was added to the solution to remove tributylamine and the excess NaH, and the solid was then filtered using a Buchner funnel. The sodium *rac*-TRISPHAT salt **3** was successively washed with CH_2Cl_2 and deionized water and dried under vacuum. Yield: 98%. ^{13}C NMR(Acetone-

d_6, 100 MHz): δ 143.0(d, Jc-p = 6.6 Hz), 123.1, 114.4(d, Jc-p = 19.8 Hz), ^{31}P NMR(Acetone-d_6, 400 MHz): δ –80.4.). ^{1}H NMR (Acetone-d_6, 400 MHz): δ 7.3(s), δ 2.1(s) (benzene and acetone residue). Using the same method, sodium *rac*-TRISPHAT salt, **3,** (97%) was also prepared from cinchonidium *rac*-TRISPHAT salt, **2.**

Synthesis of triphenylcarbenium *rac*-tris(tetra-chlorobenzenediolato)phosphate, 4.

Triphenylcarbenium *rac*-tris(tetra-chlorobenzenediolato)phosphate **4** was prepared by mixing sodium *rac*-TRISPHAT **3** (1.02 g, 1.28 mmol) and triphenylmethyl chloride (0.57 g, 2.0 mmol) in 50 mL of dry hexane and refluxing overnight. The dark brown solid was collected by filtration and washed with dry hexane and dried by vacuum. The crude product was then dissolved in dry CH_2Cl_2 and filtered through Celite to remove NaCl, followed by dry hexane addition to precipitate the dark red solids. Recrystallization from CH_2Cl_2/hexane at room temperature overnight gave dark red crystals of the trityl *rac*-TRISPHAT **4**(1.11 g). Yield: 85.7%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.18 (t, J = 8.0Hz, 3H, p-H, Ph), δ7.82 (t, J = 8.0 Hz, 6H, m-H, Ph), δ7.62 (dd, J = 8.4 Hz, J = 1.6 Hz, 6H, o-H, Ph). ^{31}P NMR (Acetone-d_6, 162 MHz): δ –80.1.

General polymerization procedures

The concentration of initiators was 0.01 M and the molecular ratio of momomer to initiator was 500:1. The polymerizations were carried at either -78ºC, -55ºC, or -50ºC and were terminated by quenching by the addition of methanol. Volatile materials were removed under vacuum and removal of residual initiator was accomplished by dissolving the crude

products in CH_2Cl_2 and precipitating in methanol solvent. The solvent was then removed under vacuum. All products were characterized by GPC and ^1H NMR and $^{13}C\{^1H\}$ NMR.

Polymerization of *tert*-butyl vinyl ether by trityl TRISPHAT, 4.

The initator was prepared by adding dry CH_2Cl_2 (0.5 mL) and dry toluene (2.5 mL) in reactor with trityl TRISPHAT **4** (0.03 mmol). When the solid dissolved, the cooled monomer (2 mL, 15.0 mmol, -78ºC) was slowly added to the solution at -78ºC. The mixture was then stirred for 3 min at -78ºC and sticky oils were produced. The polymer was purified using the method above. Yield: 35.1%. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.61 (s, 1H), δ1.65 (s, 2H), δ1.21 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 73.5(s, 1C), δ 67.9(t, 1C), δ 45.7(s, 1C), δ 29.9(s, 3C). M_w : 9693. PDI(M_w/M_n) : 1.61.

Polymerization of *tert*-butyl vinyl ether by bis(cyclopentadienyl)dimethylzirconium, 5, and trityl TRISPHAT, 4.

The initiator was prepared by mixing trityl TRISPHAT **4** (0.03 mmol) and bis(cyclopentadienyl)dimethylzirconium, **5** (0.03 mmol) in dry toluene(3 mL) and refluxing overnight. When the solid dissolved, , the cooled monomer (2 mL, 15.0 mmol, -78ºC) was slowly added in the solution at -55ºC. The mixture was then stirred for 3 min at -55ºC and a sticky oil was produced. The polymer was purified according to the above method. Yield : 73.6%. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.61 (s, 1H), δ1.66 (s, 2H), δ1.22 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 73.5 (s, 1C), δ 67.5 (t, 1C), δ 45.8 (s, 1C), δ 29.9 (s, 3C). M_w : 11618. PDI(M_w/M_n) : 1.50

Polymerization of *tert*-butyl vinyl ether by bis(cyclopentadienyl)zirconiumdichloride, 6, and sodium TRISPHAT, 3.

The initiator was prepared by mixing sodium TRISPHAT **3** (0.03 mmol) and bis(cyclopentadienyl)zirconiumdichloride **6** (0.03 mmol) in dry toluene (3 mL) and refluxing overnight. When the solid dissolved, the cooled monomer (2 mL, 15.0 mmol, -78ºC) was slowly added in the solution at -50ºC. The mixture was then stirred for 3 min at -50ºC and a sticky oils was prepared. The polymer was purified according to the above method. Yield : 76.8%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.62 (s, 1H), δ1.66 (s, 2H), δ1.22 (s, 9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 73.5 (s, 1C), δ 67.4 (t, 1C), δ 45.8 (s, 1C), δ 29.9 (s, 3C). M_w : 17630. PDI(M_w/M_n) : 1.71.

2.5. References

1. Llewellyn, D. B.; Adamson, D.; Arndtsen, B. A., *Org. Lett.* **2000,** 2, 4165-4168.
2. Nakano, T.; Okamoto, Y., *Chem. Rev.* **2001,** 101, 4013-4038.
3. Okamoto, Y.; Nakano, T., *Chem. Rev.* **1994,** 94, 349-372.
4. Mayer, S.; List, B., *Angew. Chem. Int. Ed.* **2006,** 45, 4193-4195.
5. Higashimura, T.; Sawamoto, M., *In Comprehensive Polymer Science*. Eastmond, G. C.; Ledwith, A,; Russo, S.; Sigwalt, P., Eds.; Pergamon Press: Oxoford, New York, Beijing, Frankfurt, Sao Paulo, Sydney, Tokyo, and Toronto: 1989; Vol. 3, p 673.
6. Odian, G., *Principles of Polymerization*. John Wiley & Sons, Inc.: 1991; Vol. 3, p 356.
7. Eley, D. D.; Pepper, D. C., *Trans. Faraday Soc.* **1947,** 43, 112.
8. Eley, D. D.; Richards, A. W., *Trans. Faraday Soc.* **1949,** 45, 425.
9. Lacour, J.; Ginglinger, C.; Grivet, C.; Bernardinelli, G., *Angew. Chem. Int. Ed. Engl.* **1997,** 36, 608-610.
10. Lacour, J.; Goujon-Ginglinger, C.; Torche-Haldimann, S.; Jodry, J. J., *Angew. Chem. Int. Ed. Engl.* **2000,** 39, 3695-3697.
11. Lacour, J.; Ginglinger, C.; Favarger, F.; Torche-Haldimann, S., *Chem. Commun.* **1997**, 2285-2286.
12. Lacour, J.; Ginglinger, C.; Favarger, F., *Tetrahedron Lett.* **1998,** 39, 4825-4828
13. Lacour, J.; Jodry, J. J.; Ginglinger, C.; Torche-Haldimann, S., *Angew. Chem. Int. Ed. Engl.* **1998,** 37, 2379-2380.
14. Chen, E. Y.-X.; Marks, T. J., *Chem. Rev.* **2000,** 100, 1391-1434.
15. Chien, J. C. W.; Tsai, W. M.; Rausch, M. D., *J. Am. Chem. Soc.* **1991,** 113, 8570-8571.
16. Ewen, J. A.; Elder, M. J. Eur. Pat. Appl. 0,426,637, 1991.

17. Elder, M. J.; Ewen, J. A. Eur. Pat. Appl. 0,573,403, 1993.

18. Hlatky, G. G.; Upton, D. J.; Turner, H. W. PCT Int. Appl. WO 91/09882, 1991.

19. Turner, H. W. Eur Pat. Appl. EP 0 277 004 A1, 1988.

20. Yang, X.; Stern, C.; Marks, T. J., *Organometallics* **1991,** 10, 840-842.

21. Chen, Y.-X.; Stern, C. L.; Marks, T. J., *J. Am. Chem. Soc.* **1997,** 119, 2582-2583.

22. Chen, M.-C.; Roberts, J. A. S.; Marks, T. J., *Organometallics* **2004,** 23, 932-935.

23. Coates, G. W., *Chem. Rev.* **2000,** 100, 1223-1252.

24. Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F., *Chem. Rev.* **2000,** 100, 1253-1346.

25. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F., *Angew. Chem. Int. Ed.* **1999,** 38, 428-447.

26. Gibson, V. C.; Spitzmesser, S. K., *Chem. Rev.* **2003,** 103, 283-315.

27. Ittel, S. D.; Johnson, L. K.; Brookhart, M., *Chem. Rev.* **2000,** 100, 1169-1203.

28. Bochmann, M., *Topics in Catalysis* **1999,** 7, 9 - 22

29. Sen, A., *Acc. Chem. Res.* **1988,** 21, 421-428.

30. Baird, M. C., *Chem. Rev.* **2000,** 100, 1471 - 1478.

31. Wang, Q.; Baird, M. C., *Macromolecules* **1995,** 28, 8021-8027.

32. Carr, A. G.; Dawson, D. M.; Bochmann, M., *Macromol. Rapid Commun.* **1998,** 19, 205–207.

33. Carr, A. G.; Dawson, D. M.; Bochmann, M., *Macromolecules* **1998,** 31, 2035-2040.

34. Horton, A. D., *Organometallics* **1996,** 15, 2675-2677.

35. Shaffer, T. D.; Canich, J. A. M.; Squire, K. R., *Macromolecules* **1998,** 31, 5145 - 5147.

36. Ohgi, H.; Sato, T., *Macromolecules* **1993,** 26, 559-560.

37. Ohgi, H.; Sato, T., *Macromolecules* **1999,** 32, 2403-2409.

38. Ohgi, H.; Sato, T., *Polymer* **2002,** 43.

39. Ouchi, M.; Kamigaito, M.; Sawamoto, M., *J. polym. Sci., Part A* **2001,** 39, 1060-1066.

40. Ramey, K. C.; Field, N. D.; Borchert, A. E., *J. polymer Sci., Part A* **1965,** 3, 2885-2891.

41. Higashimura, T.; Suzuoki, K.; Okamura, S., *Die Makromolekulare Chemie* **1965,** 86, 259-270.

42. Kunitake, T.; Takarabe, K., *Makromol. Chem* **1981,** 182, 817-824.

43. GomesdeMesquita, A. H.; MacGillavry, C. H.; Eriks, K., *Acta, Crystallogr.* **1965,** 18, 437-443.

44. Gust, D.; Mislow, K., *J. Am. Chem. Soc.* **1973,** 95, 1535-1547.

45. Shevchenko, I. V.; Fischer, A.; Jones, P. G.; Schmutzier, R., *Chem. Ber.* **1992,** 125, 1325-1332.

46. Lacour, J.; Bernardinelli, G.; Russell, V.; Dance, I., *CrystEngChem* **2002,** 4, 165-170.

Chapter III.

Helix-Sense Selective Polymerization of Carbodiimides by using Cationic Zirconocene Complexes possessing Chiral Counter Anions

3.1. Introduction

Many research groups are interested in developing new methods for controlling the stereoregularity of synthetic polymers and generating single handed helical polymers. One of our research goals is to develop new methods for generating single handed helical polycarbodiimides. Several factors can influence helix-sense selectivity of the polymers including the ligands on the catalyst, chiral side chains, temperature, and solvents. In ionic systems there is also the possibility of having counterion and ion pairing effects. It has recently been demonstrated that ionic interactions in metal catalysis are not only important but can be utilized to influence chirality in reaction products.[1-4] Helix-sense selective anionic polymerizations of highly isotactic vinyl polymers by chiral counterion effects have been reported.[2,3] In this study we are interested in the effects of chiral counter anions in metal-catalyzed polymerizations of achiral carbodiimides.

Robinson first reported the polymerization of carbodiimides in 1964.[5,6] However, due to the poor control over the polymerization of carbodiimide monomers, very little work was carried out. Cationic and radical initiators such as peroxides, $AlBr_3$, $Zn(Et)_2$, $B(Et)_3$, did not polymerize carbodiimides. In contrast, an anionic polymerization of the carbodiimides by using *n*-BuLi led low molecular weight polymers, the polymerization exhibited no control

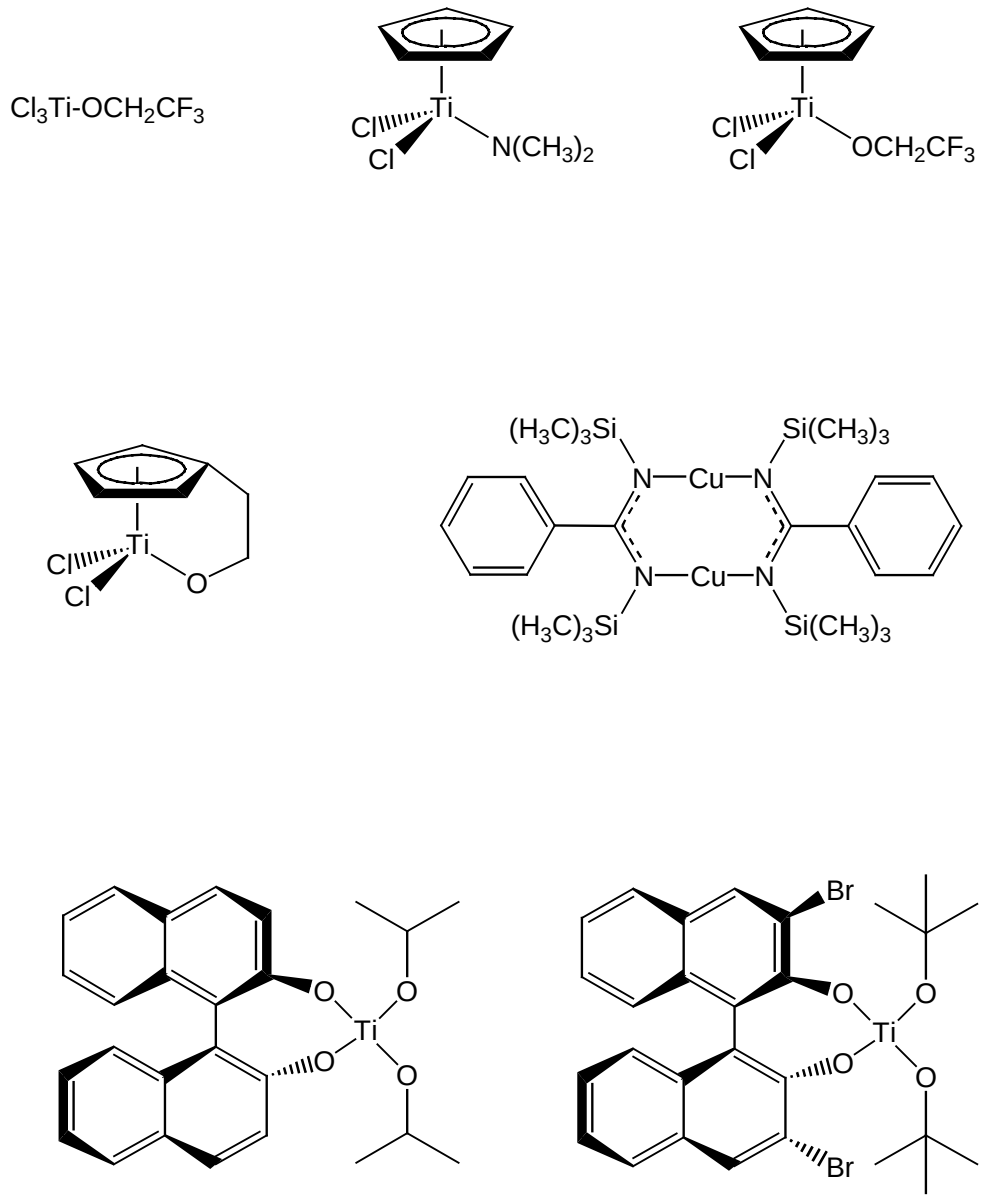


Figure 3.1. Neutral catalysts for the polymerization of carbodiimides.

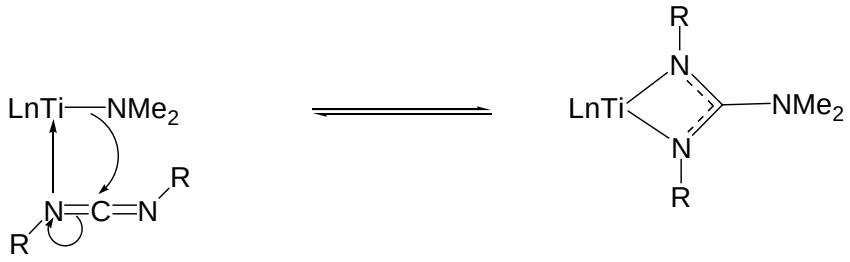
over molecular weight when the ratio of monomer to initiator was changed due to chain transfer and/or chain termination, side reactions.

Our group had a long-standing interest in designing polymerization catalysts that would allow control over the molecular weight. Many kinds of metal catalysts for polymerization of carbodiimides have been developed (Figure 3.1), the catalyst systems can control living polymerization of carbodiimides since the metal complex acts to stabilize the propagating anionic chain end resulting in a reduction in the rate of polymerization.

Goodwin used titanium(IV) based catalysts to achieve the living polymerization of many different carbodiimide monomers.[7] Subsequent research by Shibayama showed that Cu(I/II) based catalysts also initiated living polymerization of carbodiimide monomers.[8] Tian and Tang used chiral titanium(IV) based catalysts to synthesize a single handed helical polymer of achiral carbodiimide monomers.[9-13]

According to the proposed mechanism of the polymerization (Figure 3.2), the polymerization is initiated by insertion of the carbodiimide monomer into the titanium-nitrogen bond, titanium-oxygen bond, or copper-amidinate bond to form an intermediate amidinate complex. Propagation proceeds through monomer coordinations to metal active sites and insertions into metal-amidinate bond. All the steps are fully reversible. There are different ceiling temperatures of polymerization of carbodiimides depending on the side chains (i.e., 80ºC for N,N'-di-n-hexylcarbodiimide and 156ºC for N-(R/S)-(±)-(1-phenylethyl)-N'-methylcarbodiimide). The polymerization in minimum amount of solvent is favored to achieve high yield since polymerization proceeds through consecutive equilibrium reactions.

Initiation step:



Propagation step:

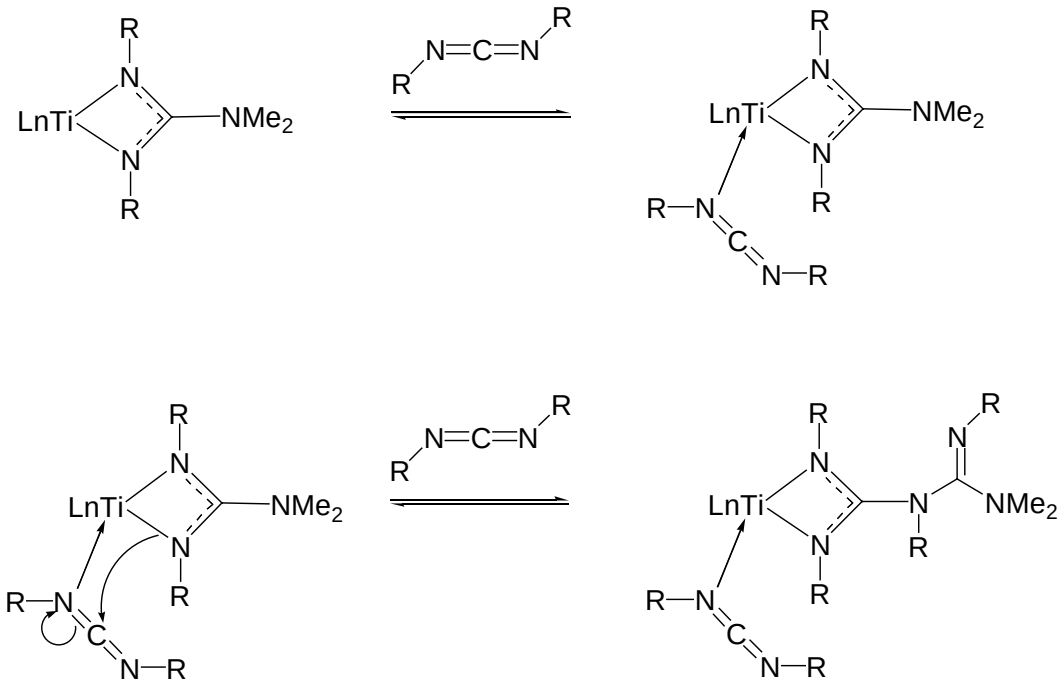
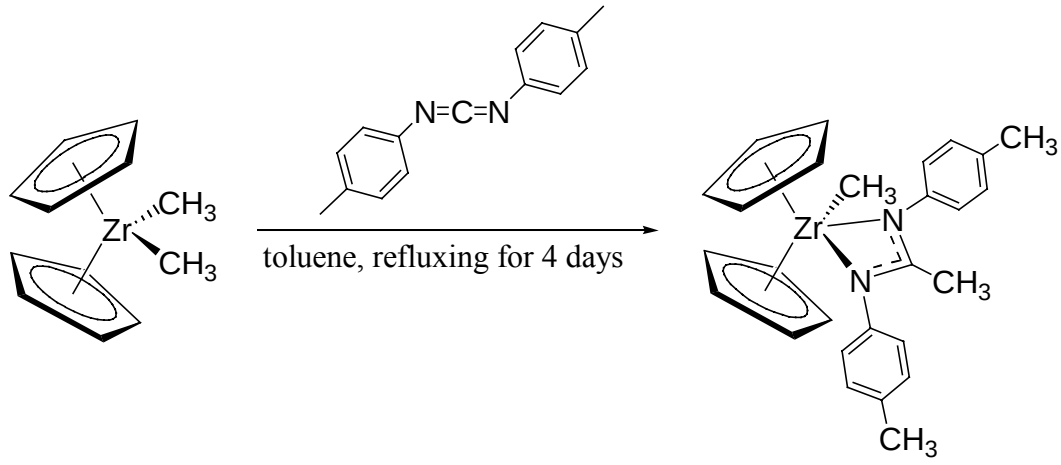


Figure 3.2. The proposed mechanism of polymerization of carbodiimide monomer using a Ti(IV) catalyst.

The metal catalysts for polymerization of carbodiimides are generally neutral and do not exist in ion-pair form. In order to study the effects of chiral counterions in metal-catalyzed polymerizations of achiral carbodiimides we need metal catalysts with ion-pair form that can polymerize carbodiimides.

According to Guastin's group, a large excess of p-tolylcarbodiimide is not polymerized by $Cp_2Zr(CH_3)_2$, only one carbodiimide molecule is inserted into the Zr-Me bonds of $Cp_2Zr(CH_3)_2$ as a consequence of the absence of a vacant coordination site in complex **I** (Figure 3.3)**.**[14]

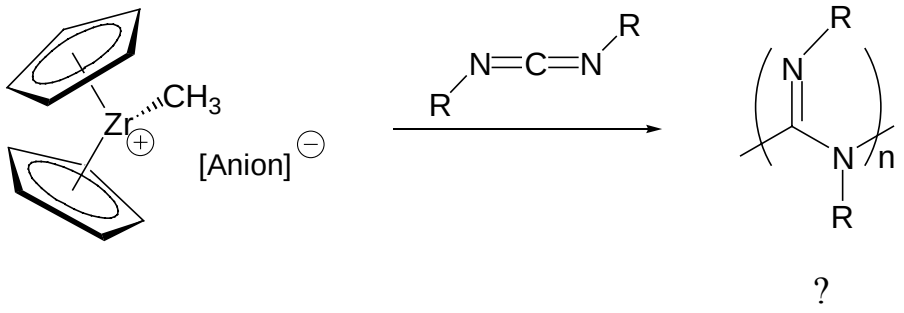


I

Figure 3.3. A single insertion of carbodiimides into Zr-Me bonds of $Cp_2Zr(CH_3)_2$.[14]

Generally activation of the $Cp_2Zr(CH_3)_2$ by using cocatalysts such as $[Ph_3C][B(C_6F_5)_4]$, leads to cationic zirconium complexes possessing counter anions such as $[Cp_2ZrCH_3][B(C_6F_5)_4]$.[15-18] We first are interested in exploring the possibility of carbodiimide polymerization by the cationic zirconocene complex (Scheme 3.1), since one

carbodiimide can be inserted into the Zr-Me bonds, the vacant coordination site can still exist and another carbodiimide can be coordinated and inserted.



Scheme 3.1. Carbodiimide polymerization by cationic zirconocene complexes.

It is important to choose the appropriate chiral counter anion and monomers for successful asymmetric polymerization. The chiral counter anion should have both configurational and chemical stability, should be a non-coordinating and non-nucleophilic anion, and should be easily separable from the reaction medium. Configurationally stable TRISPHAT anion,[19] which was synthesized and resolved, is our candidate chiral anion. In addition, it has recently been reported that a chiral TRISPHAT anion can be used to induce strong optical activity in configurationally unstable racemic cations, determine enantiomeric purities, and resolve chiral cationic complexes.[20-23] As we discussed in chapter II, our group has synthesized trityl cocatalyst possessing racemic trisphat anion, [CPh_3][*rac*-TRISPHAT], for the cationic zirconocene complex. The trisphat anion can be a non-nucleophilic anion since the trityl trisphat salt was used as an initiator for cationic polymerization and the resulting polymer was obtained in reasonable yields, and showed reasonable molecular weights.

Recently it has been reported that the asymmetric polymerization of achiral carbodiimides by using optically active catalysts possessing chiral ligands leads to single handed helical polycarbodiimides which have optical activity (Figure 3.4).[9-13,24] The polymers resulting from both chiral catalysts have opposite optical roations and show essentially mirror images in the CD spectra. Furthermore, carbodiimides with bulky substituents can help to stabilize these helical polymer conformations. Achiral carbodiimides with bulky substituents will be used to carry out helix-sense selective polymerization by the chiral counterion effect of cationic zirconocene complexes.

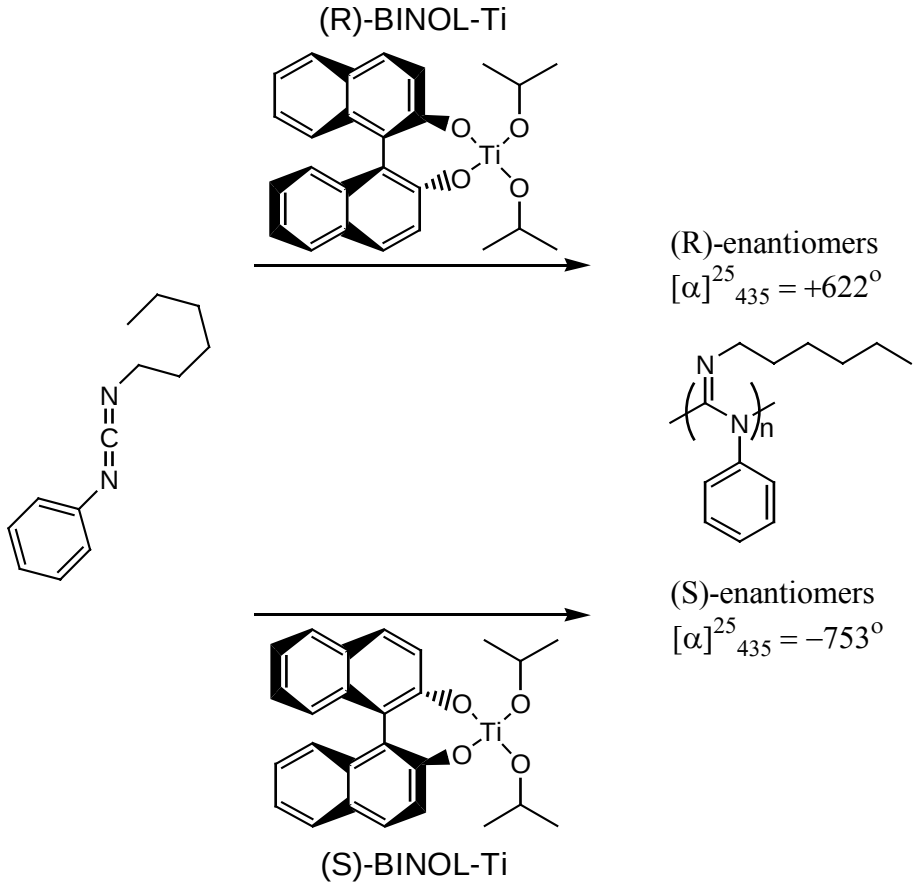
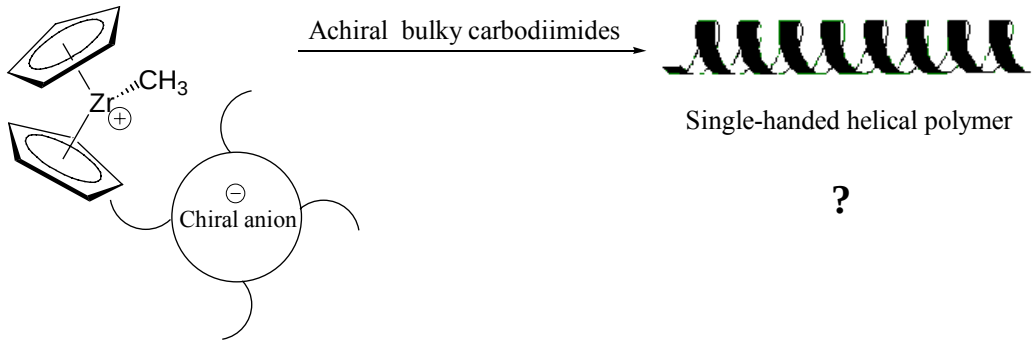


Figure 3.4. Helix-sense selective polymerization of achiral carbodiimide monomers by the chiral titanium catalysts.



Scheme 3.2. Asymmetric polymerizations of achiral carbodiimides by chiral counter anion effect.

In this research, we wish to determine whether cationic zirconocene complex can polymerize carbodiimides. (It is known from previous studies that the neutral zirconocene are not active.) If so, can these catalysts give asymmetric polymerizations of achiral carbodiimides when coupled with chiral counter anions? (Scheme 3.2) One of the ultimate goals of this work is to synthesize a helix-sense selective polymer by using cationic zirconocene complexes possessing chiral counter anions.

3.2. Results and Discussion

3.2.1. The synthesis of triphenylcarbenium *Δ*-tris(*tetra*-chlorobenzenediolato) phosphate, [CPh_3][*Δ*-TRISPHAT]

We need appropriate activators with chiral TRISPHAT anions for a helix-sense selective polymerization by using cationic zirconocene complexes possessing chiral counter

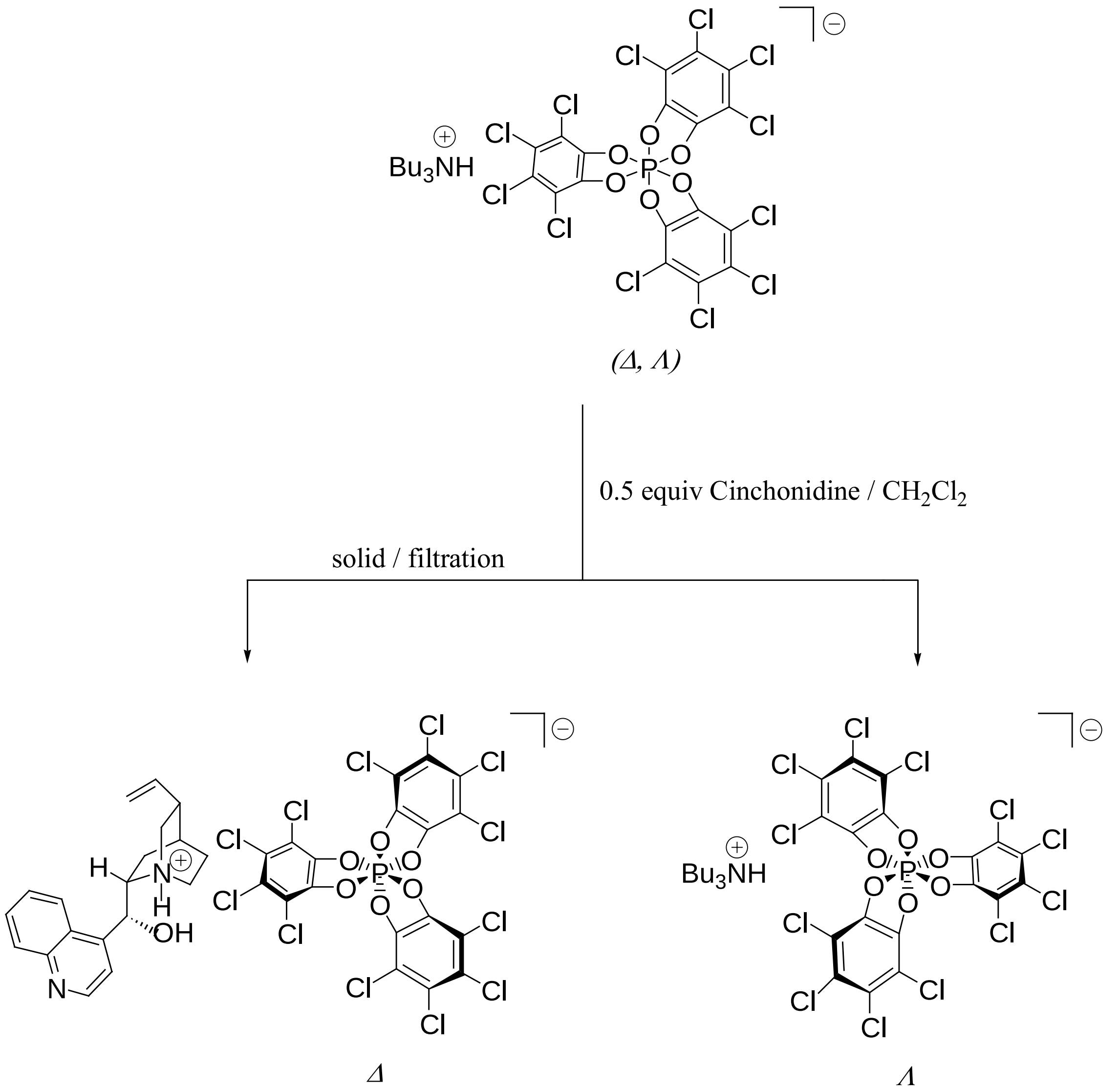


Figure 3.5. Resolution of a chiral TRISPHAT anion.[20,25]

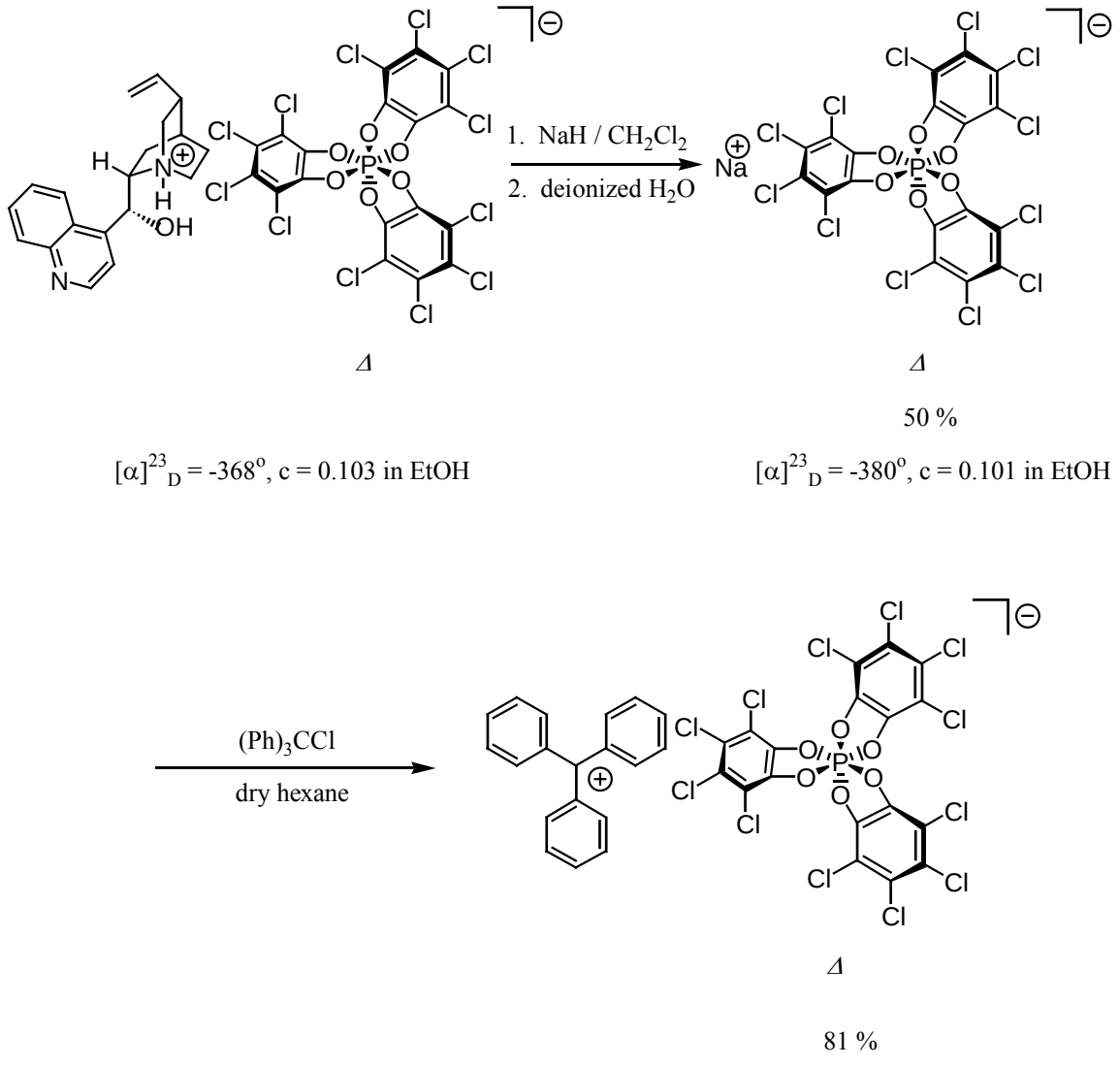


Figure 3.6. Synthesis of [CPh_3][*Δ*-TRISPHAT].

anions. As we discussed in chapter 2, trityl cocatalyst possessing *rac*-TRISPHAT anions, [CPh_3][*rac*-TRISPHAT], was synthesized by using ion exchange methods with sodium *rac*-TRISPHAT and triphenylmethyl chloride. We needed to resolve chiral TRISPHAT anion to synthesize trityl cocatalyst with chiral TRISPHAT anion.

For the resolution of chiral TRISPHAT anion, tributylammomium *rac*-TRISPHAT was prepared according to published procedures (Figure 3.5).[20,25] Addition of cinchonidine (0.5 equiv) to a CH_2Cl_2 solution of [*n*-Bu_3NH][*rac*-TRISPHAT] led to the precipitation of a white compound containing predominantly the [cinchonidinium][*Δ*-TRISPHAT] ion pair over the other diastereomer and the white compound was simply dissolved in a mixture of acetone and EtOAc, and slow evaporation of the solvents afforded pure [cinchonidinium][*Δ*-TRISPHAT]·EtOAc ($[\alpha]^{23}$ = -368º, c = 0.103 in EtOH). To remove the included solvent, the crystals can be placed under high vacuum for 2 days to give pure [cinchonidinium][*Δ*-TRISPHAT] as a white powder.

First, we needed sodium *Δ*-TRISPHAT to synthesize trityl *Δ*-TRISPHAT via a direct ion exchange method. The reaction of cinchonidinium *Δ*-TRISPHAT with sodium hydride led to sodium *Δ*-TRISPHAT (50%), which results from ion exchange by the strong base (Figure 3.6). The sodium *Δ*-TRISPHAT had a specific optical rotation of -380º (c = 0.101 in EtOH) and was characterized by ^{31}P NMR spectroscopy since the ^{31}P NMR spectra of TRISPHAT anions show a single signal in the region from δ = - 79 to – 82 ppm.

Ion exchange metathesis with sodium *Δ*-TRISPHAT and triphenylmethyl chloride (Figure 3.6) yielded the corresponding trityl *Δ*-TRISPHAT in 81% yield, which was characterized by standard spectroscopic techniques.

3.2.2. Polymerization of carbodiimide monomers by using [Cp_2ZrCH_3][*rac*-TRISPHAT] and [Cp_2ZrCH_3][*Δ*-TRISPHAT]

In order to explore the possibility of carbodiimide polymerization by the cationic zirconocene complex with *rac*-TRISPHAT anions, [Cp_2ZrCH_3][*rac*-TRISPHAT], N,N'-di-n-hexylcarbodiimide monomer was used.

The polymerization with N,N'-di-n-hexylcarbodiimide monomers (200 equiv) and [Cp_2ZrCH_3][*rac*-TRISPHAT] for 1 day at room temperature did not lead to any polymers but the polymerization at high temperature (70 ºC, for 1 day) and long polymerization time (20 ºC , for 5 days) yielded poly(N,N'-di-n-hexylcarbodiimide) in 89% and 90% yield, respectively (Figure 3.7). Generally metal-catalyzed polymerizations of carbodiimides proceeds through consecutive equilibrium reactions, with each having a ceiling temperature at which the propagation and depropagation rates are equal.[26] For an example, the ceiling temperature of polymerization with N,N'-di-*n*-hexylcarbodiimide and $CpTiCl_2N(CH_3)_2$ is 80 ºC and at higher temperatures the thermal depolymerization happens and room temperature is usually used to get high molecular weight polycarbodiimides. But in this polymerization system high temperature or long reaction time was unusually used to get high molecular weight polymers since the steric effect of the propagating site with two Cp ligands can change the polymerization rate.

When N-methyl-N'-phenylcarbodiimide was used, the polymerization (20ºC, for 3 days) yielded poly(N-methyl-N'-phenylcarbodiimide) in 92% yield (Figure 3.7). The less bulky carbodiimide monomers can improve propagation rate and make polymerization faster. Hence, cationic zirconocene complex, [Cp_2ZrCH_3][*rac*-TRISPHAT], can polymerize carbodiimides.

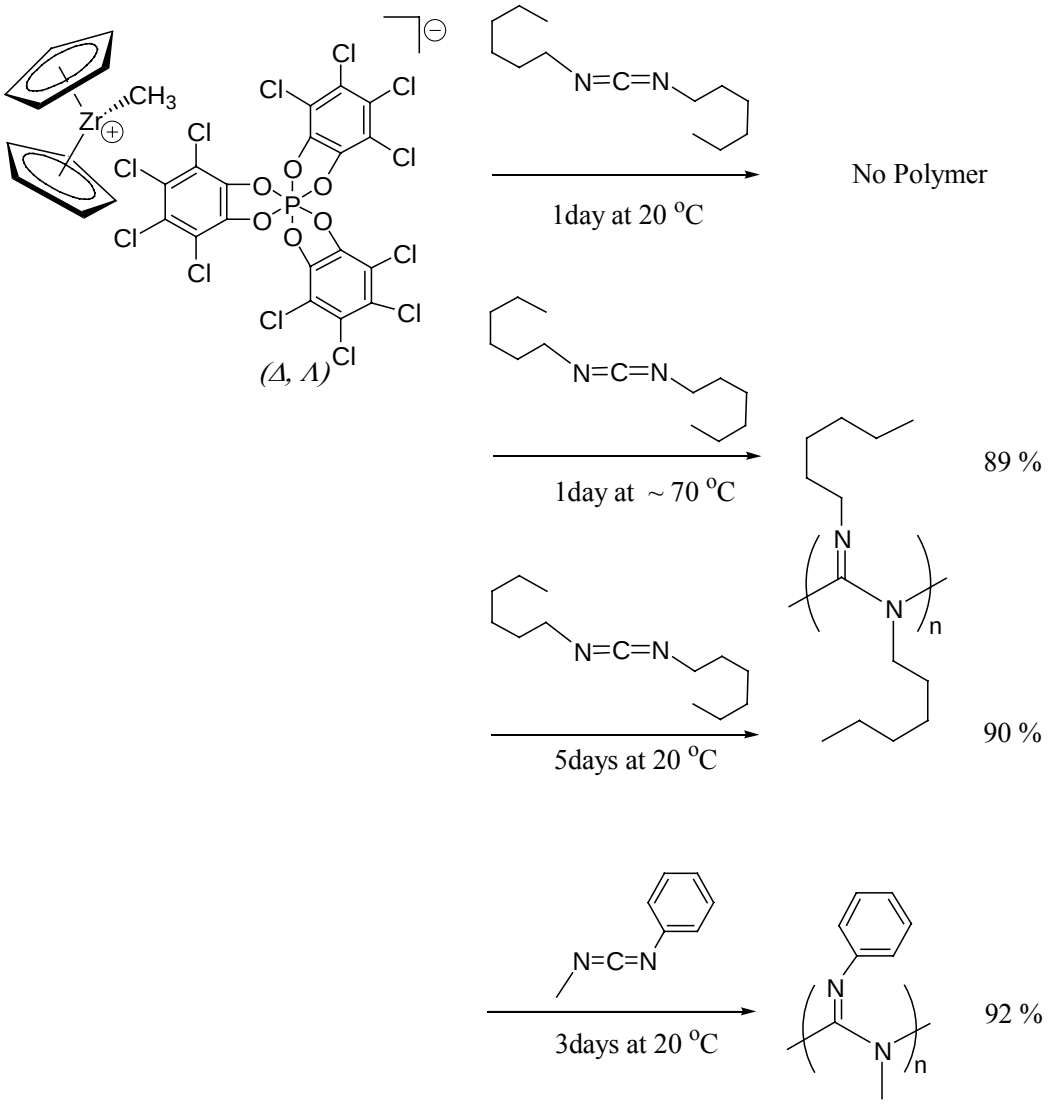


Figure 3.7. Polymerization of carbodiimides by using [Cp_2ZrCH_3][*rac*-TRISPHAT].

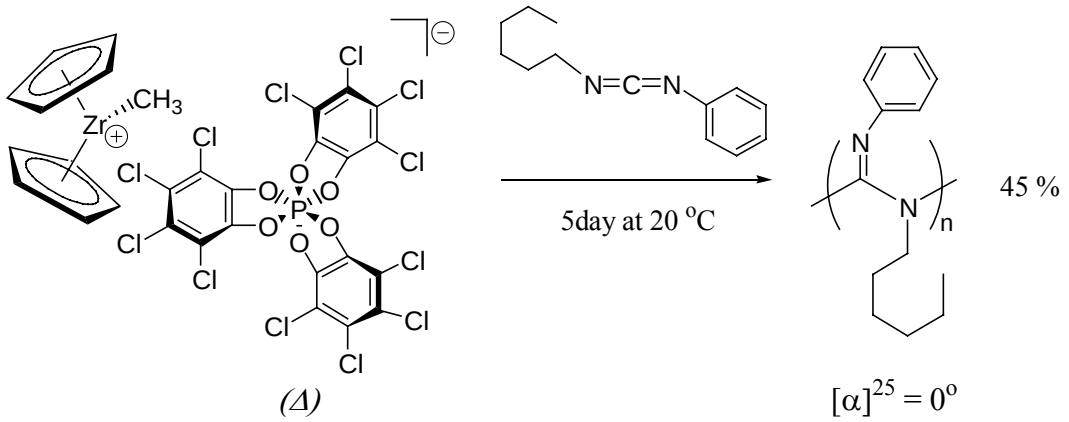
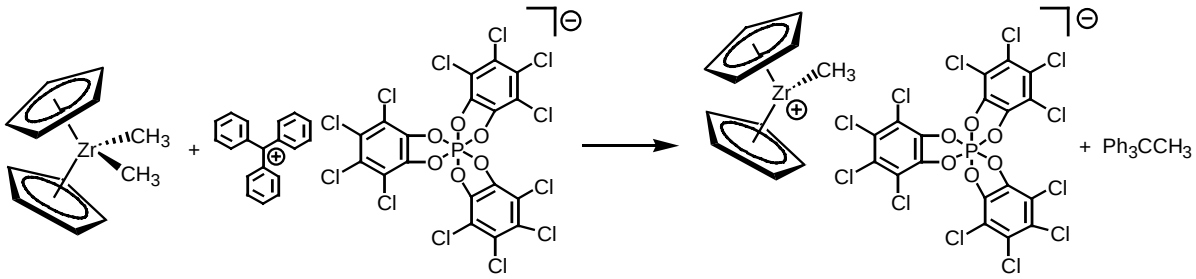


Figure 3.8. Polymerization of N-hexyl-N'-phenyl carbodiimide by using $[Cp_2ZrCH_3][\Delta$-TRISPHAT].

For helix sense selective polymerization by a cationic zirconocene complex possessing chiral counter anion, $[Cp_2ZrCH_3][\Delta$-TRISPHAT], N-hexyl-N'-phenyl carbodiimide monomer was used since asymmetry polymerization with the achiral monomer and chiral catalyst leads to a single handed helical polymer which has optical activity. The polymerization with N-hexyl-N'-phenyl carbodiimide monomers (200 equiv) and $[Cp_2ZrCH_3][\Delta$-TRISPHAT] for 5 days at room temperature yielded poly(N-hexyl-N'-phenyl carbodiimide) in 45% yield but the resulting polymers did not have optical activity (Figure 3.8). We did not observe that a chiral counter anion with a cationic catalytic site can generate single handed helical polymer in this polymerization system

3.2.3. Activating process of $Cp_2Zr(CH_3)_2$ and $[CPh_3]$[*rac*-TRISPHAT] and mechanism of $[Cp_2ZrMe]$[*rac*-TRISPHAT] catalyzed polymerization of carbodiimides by ^{1}H-NMR experiments

Cationic intermediates formed upon activation of metallocenes by cocatalysts are very important for the elucidation of the mechanism of olefin polymerization. Many research groups have been investigating the activating reactions of metallocenes and cocatalysts such as $Cp_2Zr(CH_3)_2/[CPh_3][B(C_6F_5)_4]$, using ^{1}H-NMR spectroscopy.[16-18]



1 **2** **3**

Figure 3.9. Activating process of Cp_2ZrMe_2 and $[CPh_3]$[*rac*-TRISPHAT].

In order to study the mechanism of carbodiimide polymerization we investigated the activating reaction of precatalyst $Cp_2Zr(CH_3)_2$ with cocatalyst $[CPh_3]$[*rac*-TRISPHAT] by using ^{1}H-NMR spectroscopy (Figure 3.9).

First, $Cp_2Zr(CH_3)_2$, **1**, and $[CPh_3]$[*rac*-TRISPHAT], **2**, with CD_2Cl_2 at room temperature were characterized by ^{1}H-NMR experiments respectively (Figure 3.10, Figure 3.11). When $Cp_2Zr(CH_3)_2$ and $[CPh_3]$[*rac*-TRISPHAT] (molar ratio 1:1) were mixed in

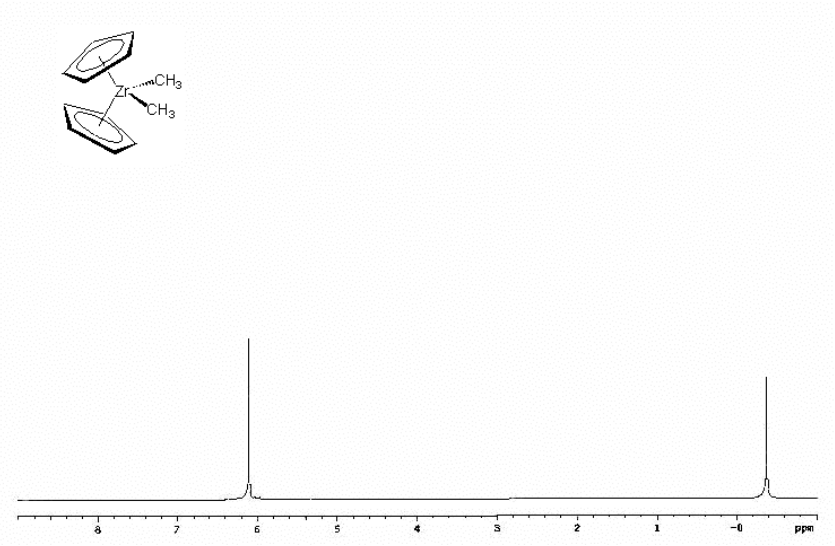


Figure 3.10. ^{1}H-NMR spectrum of $Cp_2Zr(CH_3)_2$, **1** (400 MHz, CD_2Cl_2).

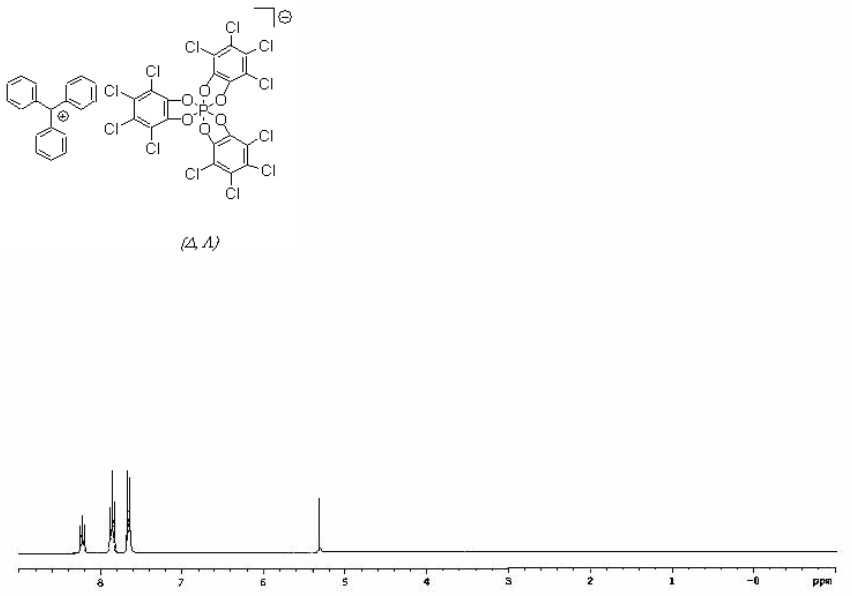


Figure 3.11. ^{1}H-NMR spectrum of [CPh_3][*rac*-TRISPHAT], **2** (400 MHz, CD_2Cl_2).

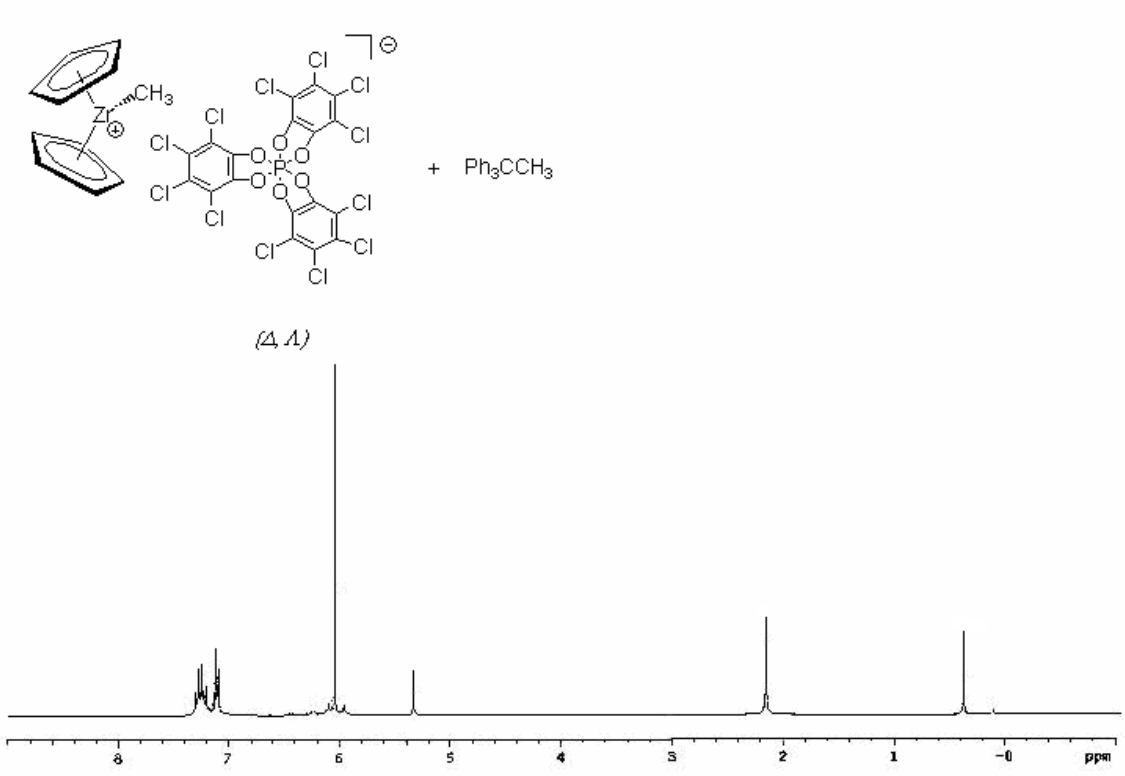


Figure 3.12. ^{1}H-NMR spectrum of a mixture of **1** and **2** (molar ratio 1:1) (400 MHz, CD_2Cl_2).

1 mL of CD_2Cl_2 at room temperature directly in a 5 mm NMR tube, a one-phase system was formed. The ^{1}H-NMR spectrum of the solution recorded 10 min after sample preparation, exhibits one patterns of cationic complex, $[Cp_2ZrCH_3]^+$ (Figure 3.12). No decomposition patterns were observed. This is in contrast to the characterization of cationic complexes of the catalytic system $Cp_2Zr(CH_3)_2$ and $[CPh_3][B(C_6F_5)_4]$ (molar ratio 1:1) in benzene-d_6 which a two-phase system was formed with an oil layer in the bottom and the ^{1}H-NMR spectrum of this mixture exhibits two different patterns of cationic complex.[16] One is cationic complex in the solution and the other is a cationic complex in the oil layer. Conversion to the mononuclear species $[Cp_2ZrCH_3]^+$ occurred only on warming but was accompanied by rapid decomposition in the chlorinated solvent.[16,17]

The reaction of an equimolecular mixture of Cp_2ZrMe_2 and $[CPh_3]$[*rac*-TRISPHAT] in CD_2Cl_2 at room temperature showed ^{1}H-NMR resonances of trityl cation, $[CPh_3]^+$, and the methyl ligand of $Cp_2Zr(CH_3)_2$ disappeared and led to the formation of the mononuclear product, [Cp_2ZrMe][*rac*-TRISPHAT], as indicated by signals for the Cp and methyl signals with relative intensities of 10:3 and evidenced by a methyl peak at δ 0.393, and the byproduct, triphenylethane as indicated by its characteristic signals.[16] This ^{1}H-NMR spectroscopic data are interpreted as evidence for the activating process of precatalyst $Cp_2Zr(CH_3)_2$ and cocatalyst $[CPh_3]$[*rac*-TRISPHAT] toward cationic zirconocene complex $[Cp_2ZrCH_3]$[*rac*-TRISPHAT] and triphenylethane.

According to the generally proposed mechanism of metal-catalyzed polymerization of carbodiimides,[7] the mechanism of the carbodiimide polymerization by $[Cp_2ZrCH_3]$[*rac*-TRISPHAT] can be proposed (Figure 3.13). First, the polymerization is initiated by insertion of the carbodiimide monomer into the Zr-CH_3 bonds to form intermediate amidinate

complex. Propagation proceeds through another carbodiimide monomer coordination to cationic zirconecene active sites and insertion into Zr-amidinate bond since the vacant coordination site can still exist.

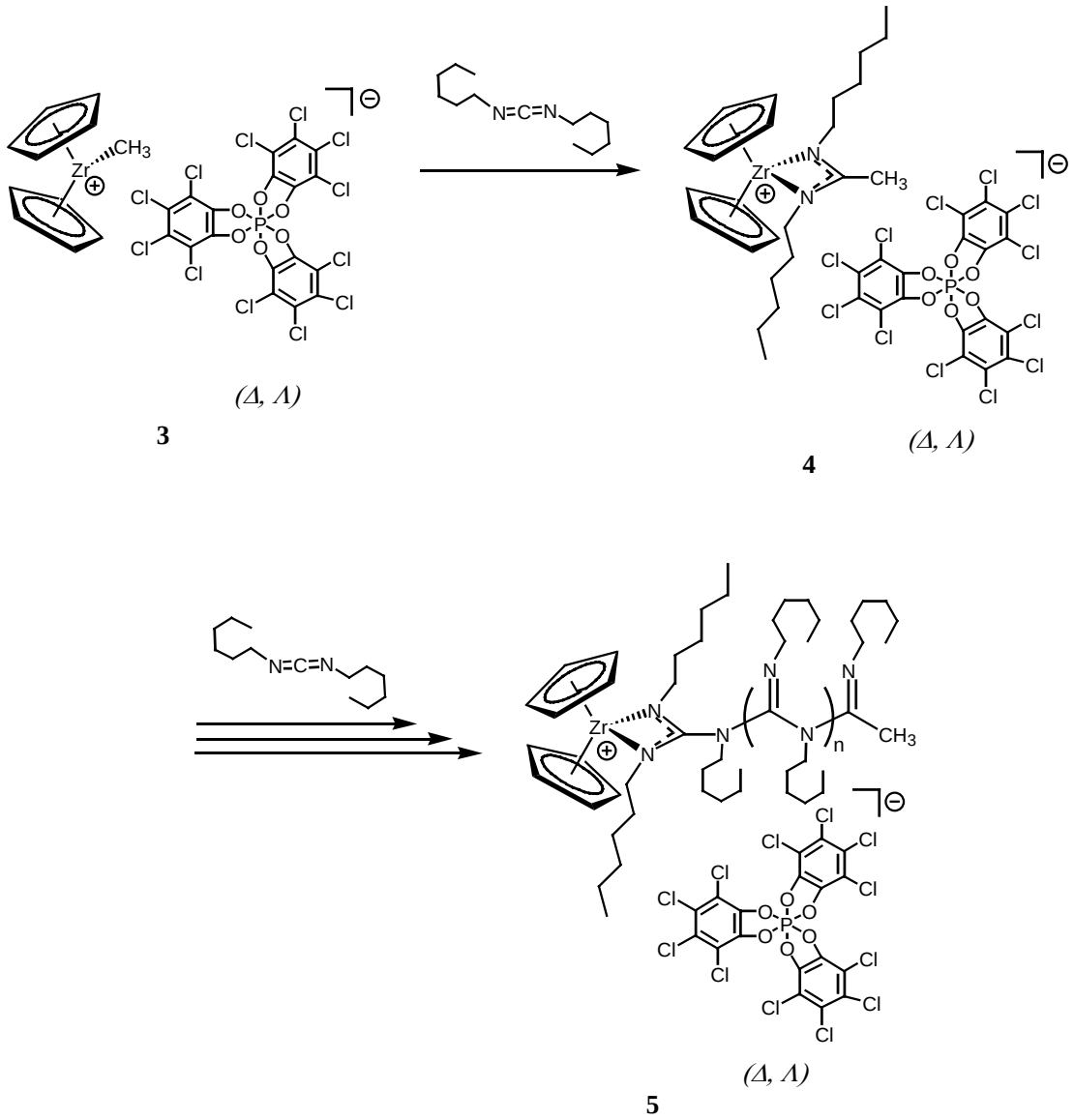


Figure 3.13. The proposed mechanism of polymerization of N,N'-di-n-hexyl carbodiimide monomer using [Cp_2ZrCH_3][*rac*-TRISPHAT] catalyst.

In order to explore the mechanism of polymerization of carbodiimide monomer using [Cp_2ZrCH_3][*rac*-TRISPHAT] catalyst, N,N'-di-n-hexyl carbodiimide monomer and ^{1}H NMR were used. When 10 equivalent N,N'-di-n-hexylcarbodiimide was added in the mixture of $Cp_2Zr(CH_3)_2$ and [CPh_3][*rac*-TRISPHAT] (molar ratio 1:1) with 1 mL of CD_2Cl_2 at room temperature, the ^{1}H-NMR spectrum of the solution recorded 10 min after sample preparation, exhibits one patterns of cationic amidinate complex (Figure. 3.14).

The reaction of 10 equivalent N,N'-di-*n*-hexylcarbodiimide with [Cp_2ZrMe][*rac*-TRISPHAT] in CD_2Cl_2 at room temperature showed ^{1}H-NMR resonances of methyl ligand of $[Cp_2ZrCH_3]^+$ disappeared and led to the formation of the amidinate complex, [Cp_2Zr{*n*-HexylNC(CH_3^*)NHexyl-*n*}][*rac*-TRISPHAT], **4**, as indicated by methyl signals of amidinate ligand at δ 1.828.[14,27,28] This ^{1}H-NMR spectroscopic data are interpreted as evidence for the initiating process of cationic zirconocene complex, [Cp_2ZrCH_3][*rac*-TRISPHAT], with carbodiimide monomers toward cationic amidinate complex, [Cp_2Zr{*n*-HexylNC(CH_3^*)NHexyl-*n*}][*rac*-TRISPHAT].

The ^{1}H-NMR spectrum of the solution recorded 3 days after sample preparation, exhibits one patterns of propagating steps by cationic catalytic sites (Figure 3.15). As the N,N'-di-*n*-hexylcarbodiimide monomers were consumed peak broadening was observed. These ^{1}H-NMR patterns are identified with general patterns of the ^{1}H-NMR spectrum of poly(N,N'-di-*n*-hexylcarbodiimide).[7,24,26] This peak broadening and ^{1}H-NMR spectroscopic data can be evidence for a propagation process through another carbodiimide monomer coordination to cationic zirconecene active sites with the vacant coordination site and insertion into Zr-amidinate bond.

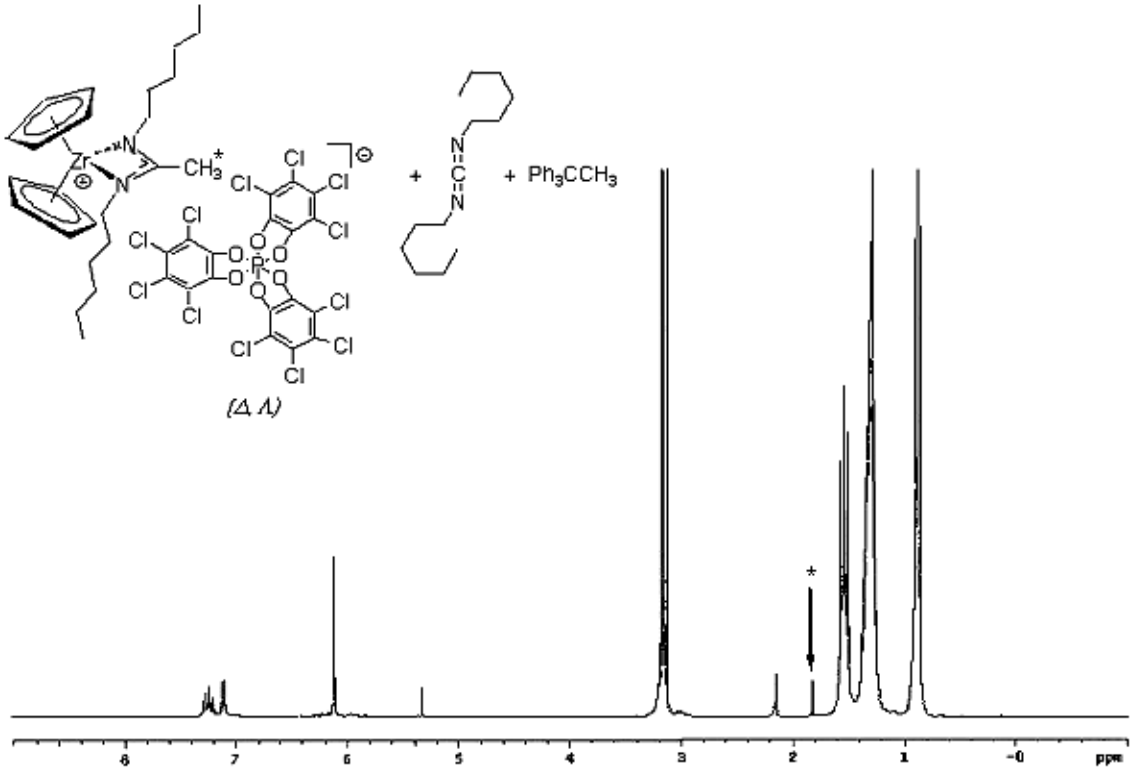


Figure 3.14. ^{1}H-NMR spectrum of 10 equiv. N,N'-di-*n*-hexylcarbodiimides in the mixture of **1** and **2** (molar ratio 1:1) (400 MHz, CD_2Cl_2, at room temperature).

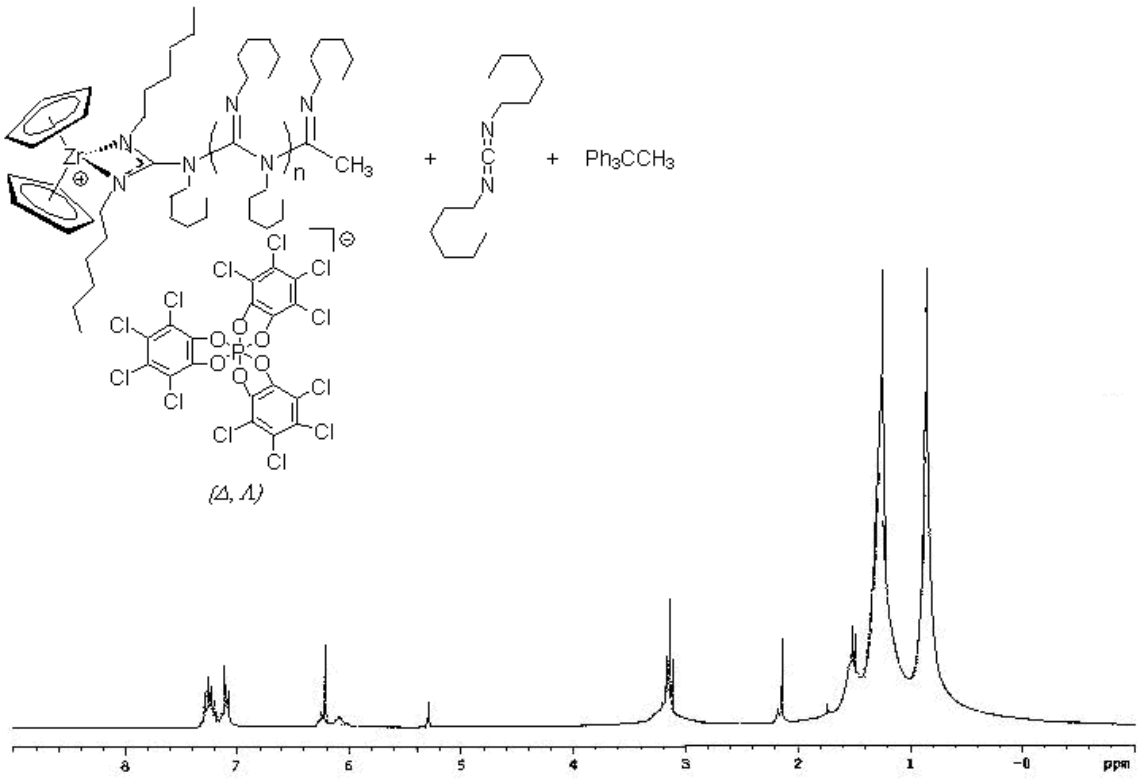


Figure 3.15. ^{1}H-NMR spectrum recorded 3 days after sample preparation (10 equiv. N,N'-di-*n*-hexylcarbodiimides in the mixture of **1** and **2** (molar ratio 1:1)) (400 MHz, CD_2Cl_2, at room temperature).

Using ^{1}H-NMR spectroscopy, a mononuclear cationic complex [Cp_2ZrCH_3][*rac*-TRISPHAT] formed in catalytic system with $Cp_2Zr(CH_3)_2$ and [CPh_3][*rac*-TRISPHAT] in CD_2Cl_2 was studied. Addition of N,N'-di-*n*-hexylcarbodiimides to the catalytic system and further ^{1}H-NMR spectroscopic monitoring showed that the catalytic system [Cp_2ZrCH_3][*rac*-TRISPHAT] initiates and polymerizes N,N'-di-*n*-hexylcarbodiimides.

3.3. Conclusions

New cocatalysts, Sodium *Δ*-tris(tetra-chlorobenzenediolato)phosphate(V) and triphenylcarbenium *Δ*-tris(tetra-chlorobenzenediolato)phosphate(V) for cationic zirconocene complexes possessing chiral counter anions were synthesized**,** respectively. The catalytic system with $Cp_2Zr(CH_3)_2$ and [CPh_3][*rac*-TRISPHAT] polymerized N,N'-di-n-hexylcarbodiimide and N-methyl-N'-phenylcarbodiimide and the resulting polymers have reasonable yields.

The asymmetry polymerization with N-hexyl-N'-phenyl carbodiimide monomers and [Cp_2ZrCH_3][*Δ*-TRISPHAT] yielded poly(N-hexyl-N'-phenyl carbodiimide) but the resulting polymers did not have optical activity. Unfortunately, we did not observe a chiral counter anion with cationic catalytic site to generate single handed helical polymer in this polymerization system.

Using ^{1}H-NMR spectroscopy, a mononuclear cationic complex [Cp_2ZrCH_3][*rac*-TRISPHAT] formed in catalytic system with $Cp_2Zr(CH_3)_2$ and [CPh_3][*rac*-TRISPHAT] in CD_2Cl_2 was studied. Addition of N,N'-di-*n*-hexylcarbodiimides to the catalytic system and further ^{1}H-NMR spectroscopic monitoring showed that the catalytic system [Cp_2ZrCH_3][*rac*-TRISPHAT] initiates and polymerizes N,N'-di-*n*-hexylcarbodiimides.

3.4. Experimental Section

General procedures and characterizations

All synthetic manipulations were conducted in either a MBraun UNILab drybox under nitrogen atmosphrere or using a Schlenk line under an inert atmosphere of nitrogen. Dry and degassed solvents (MBraun solvent system) were used throughout.

^{1}H NMR spectra were obtained at 300 MHz and 400 MHz with Varian-Mercury NMR spectrometers. Chemical shift for ^{1}H NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane and are referenced to selected residual proton peaks of the solvent as follows: $CDCl_3$, 7.27, singlet; Acetone-d_6, 2.05 quintet. Significant ^{1}H NMR data are tabulated in order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constant in Hertz, number of protons. $^{13}C\{^{1}H\}$ NMR proton decoupled NMR spectra were measured at 100 MHz on a Varian-Mercury spectrometer. Chemical shifts for $^{13}C\{^{1}H\}$ NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to selected residual peaks of the solvents as follows: $CDCl_3$, CD_2Cl_2. CD_2Cl_2 was stirred over CaH_2 overnight before being distillated and degassed. ^{31}P NMR spectra were measured at 162 MHz on a Varian-Mercury spectrometer. Chemical shifts for ^{31}P NMR spectra are reported in δ (ppm) and are referenced to a selected residual peak of the Cinchonidium TRISPHAT in acetone-d_6 solvent.

Before sample analysis, solvents were removed with a rotary evaporator and under Schlenk line vacuum (approximately 60 mTorr). Toluene, methylene dichloride, and hexane used for polymerization reactions and reactions with air and moisture sensitive materials were purified by passing through one column filled with activated A2 Alumina catalyst and

one column filled with activated Q5 copper catalyst under nitrogen atmosphere (MBraun solvent system).

All infrared spectra (cm-1) were recorded in on NaCl plates and were acquired on a JASCO FT/IR-410 spectrometer. Wavenumbers in cm-1 are reported for characteristic peaks. Optical rotations were recorded on a JASCO P-1010 polarimeter at the room temperatures. Unless otherwise noted, the specific optical rotations of cinchonidium *Δ*-TRISPHAT and sodium *Δ*-TRISPHAT were taken at 589 nm.

Experimental procedures and characterizations

Resolution Procedure of [Cinchonidium][*Δ*-TRISPHAT].

[Cinchonidium][*Δ*-TRISPHAT] was prepared according to published procedures.[20,25] A 2 L erlenmeyer flask was charged with a stirbar and 9.8 g of [tri-*n*-butylammonium][*rac*-TRISPHAT] (10.25 mmol). Dichloromethane (1 L) was added and the mixture stirred vigorously to dissolve the solid. Cinchonidine (1.51 g, 5.13 mmol, 0.5 equiv) was then added to the solution. After cinchonidine was completely dissolved, the formation of a white precipitate was observed, and the reaction was allowed to stand at room temperature for 24 h to ensure maximum precipitation. The crude reaction mixture was filtered over a Büchner funnel. The white powder, containing essentially [cinchonidinium][*Δ*-TRISPHAT], was washed with dichloromethane and collected.

At room temperature, the white powder (4.2 g) was dissolved in a minimum amount of acetone (~20 mL) and the resulting solution filtered. EtOAc (~50 mL) was added to the solution and slow evaporation of the solvents over 5 days afforded pure [cinchonidinium][*Δ*-TRISPHAT]·EtOAc (3.39 g, 3.17 mmol, 62%) as colorless plates: $[\alpha]^{23} = -368$, c = 0.103 in

EtOH. ^{31}P NMR (162 MHz, acetone-d_6): δ (ppm) -79.4; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.91 (d, 1H), 8.21 (d, 1H), 8.09 (d, 1H), 7.79 (d, 1H), 7.75 (dd, 1H), 7.58 (dd, 1H), 6.29 (br, 1H), 5.83 (ddd, 1H), 5.06 (2d, 2H), 6.31 (dd, 1H), 4.47 (ddd, 1H), 4.12 (dddd, 1H), 3.93 (dd, 1H), 3.63 (dd, 1H), 3.62 (dddd, 1H), 3.3-2.5 (br, 2H, OH and NH+), 2.38 (dd, 1H), 2.31 (ddd, 1H), 2.23 (dd, 1H), 2.10 (dddd, 1H), 1.84 (dddd, 1H).

Synthesis of sodium *Δ*-TRISPHAT and trityl *Δ*-TRISPHAT.

1.5 equivalent sodium hydride was added to cinchonidium *Δ*-TRISPHAT salt (3.00 g, 2.8 mmol) in 100 mL of CH_2Cl_2. The mixture was then stirred for 12 h at room temperature during which time a white solid precipitated. Deionized water (100 mL) was added to the solution to remove cinchonidine and the excess NaH. The solid was filtered using a Buchner funnel. The solid was successively washed with CH_2Cl_2 and deionized water and dried under vacuum. Yield: 1.11 g (50%). $[\alpha]^{23}$ = -380, c = 0.101 in EtOH ^{13}C NMR (Acetone-d_6, 100 MHz): δ (ppm) 143.0 (d, Jc-p = 6.6 Hz), 123.1, 114.4 (d, Jc-p = 19.8 Hz), ^{31}P NMR (Acetone-d_6, 162 MHz): δ (ppm) –80.4.). ^{1}H NMR (Acetone-d_6, 400 MHz): δ (ppm) 7.3(s), 2.1(s) (benzene and acetone residue). Trityl *Δ*-TRISPHAT was prepared by mixing sodium *Δ*-TRISPHAT (1.02 g, 1.28 mmol) and triphenylmethyl chloride (0.57 g, 2.0 mmol) in 50 mL of dry hexane and refluxing overnight. The dark brown solid was collected by filtration and washed with dry hexane and dried by vacuum. The crude product was then dissolved in dry CH_2Cl_2 and filtered through Celite to remove NaCl, followed by dry hexane addition to precipitate the dark red solids (1.05 g). Yield: 81.0%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) 8.18 (t, J = 8.0Hz, 3H, p-H, Ph), 7.82 (t, J = 8.0 Hz, 6H, m-H, Ph), 7.62 (dd, J = 8.4 Hz, J = 1.6 Hz, 6H, o-H, Ph). ^{31}P NMR (Acetone-d_6, 162 MHz): δ (ppm) –80.1.

Synthesis of N,N'-di-*n*-hexylurea.

A 250 mL round bottom flask was charged with 10.0 mL hexylisocyanate (8.95 g, 70.3 mmol), a magnetic stir bar, and 150 mL reagent grade methylenedichoride. The resulting solution was cooled to 0 ºC by the use of an ice bath and covered with a septum. 9.29 mL 1-aminohexane (7.12 g, 70.3 mmol) was added by using a syringe with stirring to the solution under nitrogen at 0 ºC for 30 minutes. The resultant solution was stirred for an additional 1 hour at room temperature after the addition of the 1-aminohexane. The solvent was removed by rotary evaporator at 50 ºC. Yield: 16.0 g (70 mmol, 100%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 4.35 (br s, 2H, NH), 3.14 (m, 4H, CH_2N), 1.47 (m, 4H, CH_2), 1.25 (m, 12H, $CH_2CH_2CH_2$), 0.87 (t, 6H, CH_3)

N-methyl-N'-phenylurea.

The same procedure for the preparation of N, N'-di-n-hexylurea was employed. The quantities of reagents used were 3.00 mL methylisocanate (2.90 g, 50.9 mmol), 4.63 mL aniline (4.73 g, 50.9 mmol), and 100 mL $CHCl_3$. Yield: 6.0 g (40.0 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.05 (m, 1H, aromatic), 7.27 (m, 4H, aromatic), 2.80 (s, 3H, CH_3).

N-*n*-hexyl-N'-phenylurea.

The same procedure for the preparation of N, N'-di-n-hexylurea was employed. The quantities of reagents used were 24.11 g phenyl isocyanate (0.2 mol), 20.2 g hexylamine (0.2 mol), and 100 mL CH_2Cl_2. Yield: 38.55 g (0.17 mol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ

(ppm) 7.05 (m, 1H, aromatic), 7.27 (m, 4H, aromatic), 3.20 (br s, 2H, NH), 1.46 (m, 2H, CH_2), 1.26 (m, 8H, $CH_2CH_2CH_2CH_2$), 0.86 (t, 3H, CH_3).

Synthesis of N,N'-di-*n*-hexylcarbodiimide.

The carbodiimides were prepared similarly with a slight modification of literature procedures.[29] A dry 500 mL round bottom flask was charged with 250 mL CH_2Cl_2, 20.6 g triphenylphosphine (78.5 mmol, 25% excess), and a stir bar. A dry pressure equalizing addition funnel was charged with 30 mL CH_2Cl_2 and 4.04 mL bromine (12.5 g, 78.5 mmol, 25% excess) and was then placed on the 500 mL round bottom flask. the triphenylphosphine solution was cooled by an ice bath and stirred vigorously under nitrogen. The bromine solution was added dropwise over the course of 30 minutes, and the resulting solution was allowed to stir for an additional 10 minutes. Dibromotriphenylphosphorane was suspended in the solution and 22.1 mL triethylamine (16.0 g, 158 mmol, 26% excess) was added to it. 14.34 g N,N'-di-n-hexylurea (62.80 mmol) was added in five equivalent portions to the 0 ºC suspension over the next hour. One hour after the last addition of the urea, 100 mL of water was added to the round bottom flask in order to extract the triethylammonium hydrochloride, and the organic and aqueous phases were separated using a separatory funnel. The dichloromethane solution, after drying over sodium sulfate, was reduced to approximately 50 mL by the use of a rotary evaporator. Addition of 300 mL pentane to the viscous, dark brown oil served to precipitate the triphenylphosphine oxide. The white precipitate was then vacuum filtered through a 60 mL medium-porosity sintered glass funnel and the solution was reduced to approximately 40 mL by using a rotary evaporator and the solvent was evaporated by using a slow stream of nitrogen for 2 hours. The desired product, a clear, colorless oil,

was obtained by distillation under reduced pressure. Yield: 8.5 g (40.4 mmol, 64%); IR: 2131 (s, N=C=N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.14 (t, 4H), 1.50 (tt, 4H), 1.23 (m, 12H), 0.82 (t, 6H).

N-methyl-N'-phenylcarbodiimide.

The same procedure for the preparation of N,N'-di-*n*-hexylcarbodiimide was employed. The quantities of reagents used were 6.0 g N-methyl-N'-phenylurea (40.0 mmol), 13.11 g triphenylphosphine (50.0 mmol, 1.25 eq), 2.57 mL bromine (50.0 mmol, 1.25 eq) and 14.4 mL triethylamine (104.0 mmol, 2.6 eq). Distillation: 50 °C, 0.1 Torr. Yield: 3.5 g (26.6 mmol, 66%); IR: 2142 cm^{-1} (s, N=C=N). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.00 (m, 5 H, C_6H_5), 3.23 (s, 3H, CH_3).

N-(n-hexyl)-N'-phenylcarbodiimide.

The same procedure for the preparation of N,N'-di-*n*-hexylcarbodiimide was employed. The quantities of reagents used were 38.0 g N-n-hexyl-N'-phenylurea (0.17 mol), 65 g triphenylphosphine (0.25 mol, 1.47 eq), 13 mL bromine (0.25 mol, 1.47 eq) and 70 mL triethylamine (0.5 mol, 2.9 eq). Distillation: 90 °C, 0.1 Torr. Yield: 31 g (72.1%). IR: 2131 (s, N=C=N). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (m, 3H), 7.07 (m, 2H), 3.40 (t, 2H), 1.67 (m, 2H), 1.41 (m, 2H), 1.31 (m, 4H), 0.88 (t, 3H).

General Procedures for Polymerization

All synthetic manipulations were conducted in either a Vacuum atmospheres glovebox or using a Schlenk line under an inert atmosphere of nitrogen. Dry, oxygen-free solvents were used throughout.

The catalyst was prepared in the glove box by adding a solution of bis(cyclopentadienyl)dimethylzirconium (1 equiv) in dry methylene dichloride, precooled to -75º C, to a solution of [Ph_3C][TRISPHAT] (1 equiv) in dry methylene dichloride, also precooled to –78º C. Carbodiimide monomers (200 equiv) were then added to the yellow catalyst solution at room temperature and the polymerization was quenched by the addition of methanol and the volatiles removed in *vacuo*. . The resultant polymers were purified, by precipitation into excess methanol after crude polymers were dissolved to toluene. The solvent was then removed under vacuum. All products were characterized by ^{1}H NMR and ^{13}C NMR.

Polymerization of N,N'-di-*n*-hexylcarbodiimides by bis(cyclopentadienyl) dimethylzirconium and trityl *rac*-TRISPHAT .

Dry CH_2Cl_2 (3 mL) was added in trityl *rac*-TRISPHAT (0.03 mmol) and bis(cyclopentadienyl)dimethylzirconium (0.03 mmol) at -78 ºC. When the solids were dissolved completely, the N,N-di-*n*-hexylcarbodiimide (1.26 g, 6.0 mmol) was slowly added in the solution at room temperature. Two different reaction conditions were used. One is the mixture was stirred for 5days at room temperature and sticky oil was produced. The other is the mixture was stirred for 3days at 70 ºC. The polymers were purified according to the above method. The yields were 90.0% (1.13 g) and 89.0% (1.12 g), respectively. IR: 1648

(s, guanidine stretching); ^{1}H NMR (400 MHz, $CDCl_3$) d: 4.00-4.20 (br), 2.80-3.20 (br), 1.00-1.47 (br), 0.60-1.00 (br); ^{13}C NMR (100 MHz, $CDCl_3$) d: 48.76, 32.34, 31.92, 29.17, 27.73, 22.92, 14.14.

Poly(N-methyl-N'-phenylcarbodiimide).

The same procedure for the preparation of poly(N,N'-di-*n*-hexylcarbodiimide) was employed. 0.79 g (6.0 mmol) of N-methyl-N'-phenylcarbodiimide was used. The mixture was stirred for 3days at room temperature. Yield: 0.73 g (92.0%); ^{1}H NMR (400 MHz, CDCl3) d: 7.2-6.4 (br), 2.8-3.5(br).

Polymerization of N-(*n*-hexyl)-N'-phenylcarbodiimides by bis(cyclopentadienyl) dimethylzirconium and trityl *Δ*-TRISPHAT.

Dry CH_2Cl_2 (3 mL) was added in trityl *Δ*-TRISPHAT (0.03 mmol) and bis(cyclopentadienyl)dimethylzirconium (0.03 mmol) at -78 ºC. When the solids were dissolved completely, the N-(*n*-hexyl)-N'-phenylcarbodiimide (1.21 g, 6.0 mmol) was slowly added in the solution at room temperature. The mixture was then stirred for 5days at room temperature and sticky oil was produced. The polymer was purified according to the above method. Yield: 0.5 g (45.0%); IR: 1624 (s, guanidine stretching); ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 7.2-6.4 (br), 2.8-3.6(br), 1.2-0.2 (br); ^{13}C NMR (100 MHz, CDCl3): δ (ppm) 148.5, 148.2, 128.3, 122.1, 47.3, 31.8, 28.3, 26.3, 23.0, 14.4.

^{1}H-NMR Experiments for studies of Activating process of $Cp_2Zr(CH_3)_2$ and [CPh_3][*rac*-TRISPHAT] and mechanism of [Cp_2ZrMe][*rac*-TRISPHAT] catalyzed polymerization of carbodiimides.

All manipulations were performed under nitrogen using standard Schlenk techniques. CD_2Cl_2 was stirred over CaH_2 overnight before being distillated and degassed by several freeze-thaw cycles.

$Cp_2Zr(CH_3)_2$ (1.2 mg, 4.9 μmol) and [CPh_3][*rac*-TRISPHAT] (5.0 mg, 4.9 μmol) were mixed with 1 mL of CD_2Cl_2 at room temperature and the mixed solution was then transferred in a air-free NMR tube. The ^{1}H NMR spectrum of the [Cp_2ZrMe][*rac*-TRISPHAT] solution; ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 6.03 (s, 10H, C_5H_5), 0.39 (s, 3H, $ZrCH_3$). Ph_3CCH_3: ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 7.23-7.16 (m, 9H, *m, p*-C_6H_5), 7.09 (m, 6H, *o*-C_6H_5), 2.16 (s, 3H, $(C_6H_5)_3CC\mathit{H}_3$).

The ^{1}H-NMR spectrum of the solution recorded 10 min after N,N-di-*n*-hexylcarbodiimide (0.01 mg, 49 μmol) was added in the sample solution is Figure 3.14.

The ^{1}H-NMR spectrum of the solution recorded 3 days after sample preparation is Figure 3.15.

3.5. References

1. Llewellyn, D. B.; Adamson, D.; Arndtsen, B. A., *Org. Lett.* **2000,** 2, 4165-4168.
2. Okamoto, Y.; Nakano, T., *Chem. Rev.* **1994,** 94, 349-372.
3. Nakano, T.; Okamoto, Y., *Chem. Rev.* **2001,** 101, 4013-4038.
4. Mayer, S.; List, B., *Angew. Chem. Int. Ed.* **2006,** 45, 4193-4195.
5. Robinson, G. C., *J. Polym. Sci. A* **1964,** 2, (3901-3908).
6. Robinson, G. U. S. Patent. 3,200,087, 1965.
7. Goodwin, A.; Novak, B. M., *Macromolecules* **1994,** 27, 5520-5522.
8. Shibayama, K.; Seidel, S. W.; Novak, B. M., *Macromolecules* **1997,** 30, 3159-3163.
9. Tian, G.; Lu, Y.; Novak, B. M., *Polymer Preprints* **2003,** 44, (2), 693-694.
10. Tian, G.; Lu, Y.; Novak, B. M., *J. Am. Chem. Soc.* **2004,** 126, 4082-4083.
11. Tang, H.-Z.; Boyle, P. D.; Novak, B. M., *J. Am. Chem. Soc.* **2005,** 127, 2136-2142.
12. Tang, H.-Z.; Lu, Y.; Tian, G.; Capracotta, M. D.; Novak, B. M., *J. Am. Chem. Soc.* **2004,** 126, 3722-3723.
13. Tang, H.-Z.; Novak, B. M.; He, J.; Polavarapu, P. L., *Angew. Chem. Int. Ed.* **2005,** 44, 7298-7301.
14. Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C., *Inorg. Chem.* **1985,** 24, (5), 654-660.
15. Chen, E. Y.-X.; Marks, T. J., *Chem. Rev.* **2000,** 100, 1391-1434.
16. Talsi, E. P.; Eilertsen, J. L.; Ystenes, M.; Rytter, E., *J. Organomet. Chem.* **2003,** 677, 10-14.
17. Lancaster, S. J.; Bochmann, M., *J. Organomet. Chem.* **2002,** 654, 221-223.

18. Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M., *J. Am. Chem. Soc.* **2001,** 123, 223-237.

19. Lacour, J.; Ginglinger, C.; Grivet, C.; Bernardinelli, G., *Angew. Chem. Int. Ed. Engl.* **1997,** 36, 608-610.

20. Lacour, J.; Ginglinger, C.; Favarger, F., *Tetrahedron Lett.* **1998,** 39, 4825-4828

21. Lacour, J.; Ginglinger, C.; Favarger, F.; Torche-Haldimann, S., *Chem. Commun.* **1997**, 2285-2286.

22. Lacour, J.; Goujon-Ginglinger, C.; Torche-Haldimann, S.; Jodry, J. J., *Angew. Chem. Int. Ed. Engl.* **2000,** 39, 3695-3697.

23. Lacour, J.; Jodry, J. J.; Ginglinger, C.; Torche-Haldimann, S., *Angew. Chem. Int. Ed. Engl.* **1998,** 37, 2379-2380.

24. Lu, Y. Ph.D. Thesis. North Carolina State University, 2005.

25. Favarger, F.; Goujon-Ginglinger, C.; Monchaud, D.; Lacour, J., *J. Org. Chem.* **2004,** 69, 8521-8524.

26. Goodwin, A. Ph.D. Thesis. University of California at Berkeley, 1996.

27. Jayaratne, K. C.; Sita, L. R., *J. Am. Chem. Soc.* **2000,** 122, 958-959.

28. Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R., *J. Am. Chem. Soc.* **2001,** 123, 6197-6198.

29. Palomo, C.; Mestres, R., *Synthesis* **1981**, 373.

Chapter IV.

Progress toward Chiral Zirconium Complexes for Asymmetric α-olefin Polymerization

4.1. Introduction

Many research groups are interested in developing new methods for controlling the stereoregularity of synthetic polymers and generating single handed helical polymers. One of the most challenging areas is the synthesis of single handed helical poly(α-olefins) by asymmetric coordination-insertion polymerization of α-olefins. We are interested in discovering new chiral catalysts for generating highly tactic, single handed helical poly(α-olefins).

In order to approach this research, we needed to synthesize new catalysts for polymerization of sterically bulky α-olefins (such as vinylcyclohexane) to prevent racemization through main chain bond rotation of single handed helical poly(α-olefins). The catalysts and monomers should yield highly stereoregular polymers and the polymers should have helical conformations and the catalysts should possess chirality to select for a preferred helical sense.

There are many kinds of catalysts for α-olefin polymerization, from early transition metal (d^0) to late transition metal (d^8) catalysts.[1-8] Generally single site metal (d^0) catalysts are used for precise stereoregular control of polypropylenes such as the group IV metallocene catalysts of titanium, zirconium, and hafnium.[1,2,7] One of the important reasons is the metal-olefin interaction is highly unstable and remains very weak since there are no electrons in d orbitals for π back bonding from a d^0 system into the empty π* orbitals of the olefin (figure 4.1).[9] For example, recently an alkene coordinated to the metal (d^0) has directly been

observed at -130 ºC by Casey's group.[10] The bonding nature of d^0 metal-alkene complexes are so weak that the structural parameters pertaining to the coordination of the olefin are of particular importance.[11,12] The particular structure of d^0 metal catalysts can control the stereoregularity of poly(α-olefin)s, leading to isotactic, syndiotactic polymers, and so on. In order to approach this research goal, d^0 metals will be used for synthesis of new chiral catalyst.

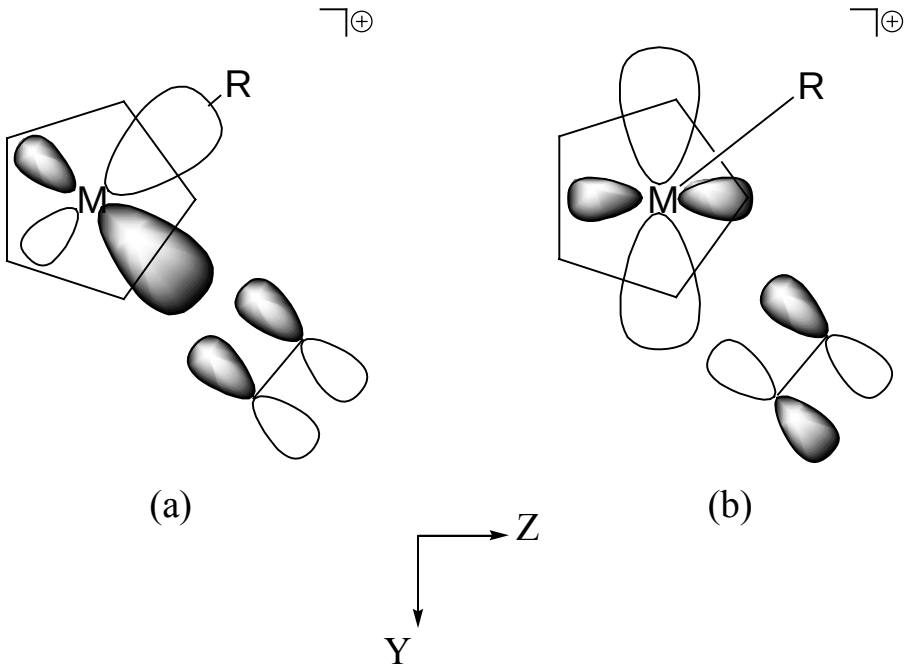
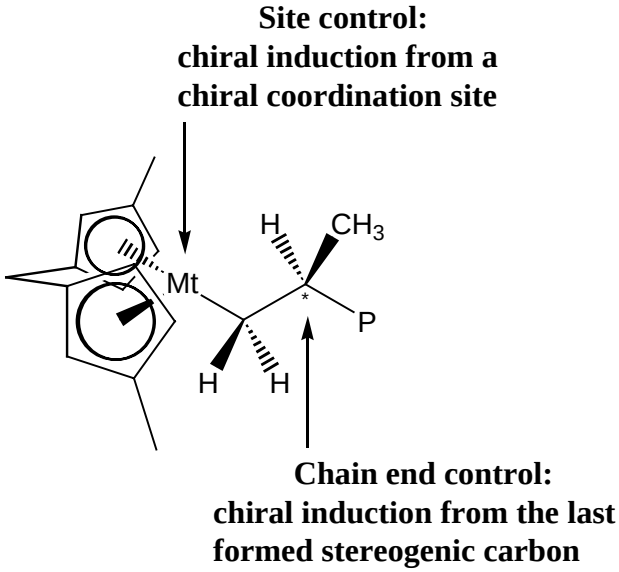


Figure 4.1. Schematic representation of the σ-interaction of a $[Cp_2M(d^0)R]^+$ fragment (viewed from the top) with incoming olefin (a). The stabilizing π-back bonding into the empty π* orbitals of the olefin (b) is not possible due to lack of electrons in a d^0 system.[9]



Scheme 4.1. Two possible sources of enantioface selectivity in olefin insertion.

There are two possible sources of enantioface selectivity in olefin insertion by the structural parameters pertaining to the coordination of the olefin.[2,7,11] One is enantiomorphic site control where the chiral induction comes from a chiral coordination site. The other is chain-end control where the chiral induction comes from the new stereogenic carbon which every monomer insertion generates (Scheme 4.1).

The two enantiomorphic site controls (isospecific and syndiospecific site control), induced by the chiralities of the catalyst active site can be more effective, with the differences in activation energy ($\Delta\Delta E^{\ddagger}_{enant} = \Delta E^{\ddagger}_{si} - \Delta E^{\ddagger}_{re}$) for the insertion of the two enantiofaces up to 5 kcal/mol (Figure 4.2).[2,7,11-14] Resconi and coworkers showed the experimental $\Delta\Delta E^{\ddagger}$ values and calculated $\Delta\Delta E^{\ddagger}$ values for enantioface selectivity of several

different zirconocenes such as *rac*-[ethylene(1-indenyl)$_2$]ZrCl$_2$ ($\Delta\Delta E^{\ddagger}_{enant}$ = 3.3 ± 0.2 kcal/mol, obsd, $\Delta\Delta E^{\ddagger}_{enant}$ = 3.5 kcal/mol, cald) and the $\Delta\Delta E^{\ddagger}$ values are changed depending on ligand structures.[2,15] As the value of $\Delta\Delta E^{\ddagger}_{enant}$ increases, the stereoregularity of the poly(α-olefin)s increases.

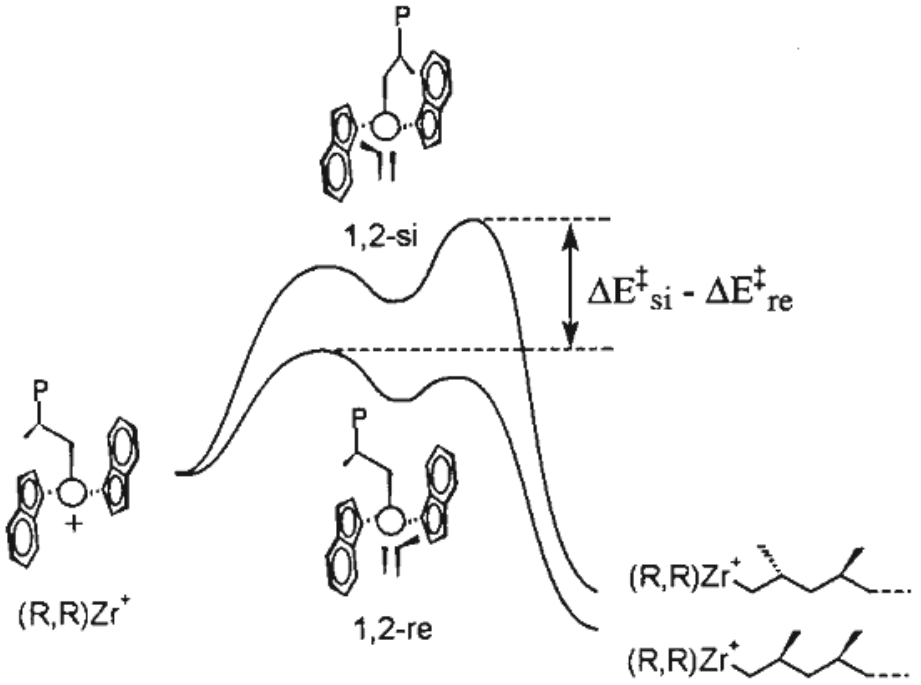
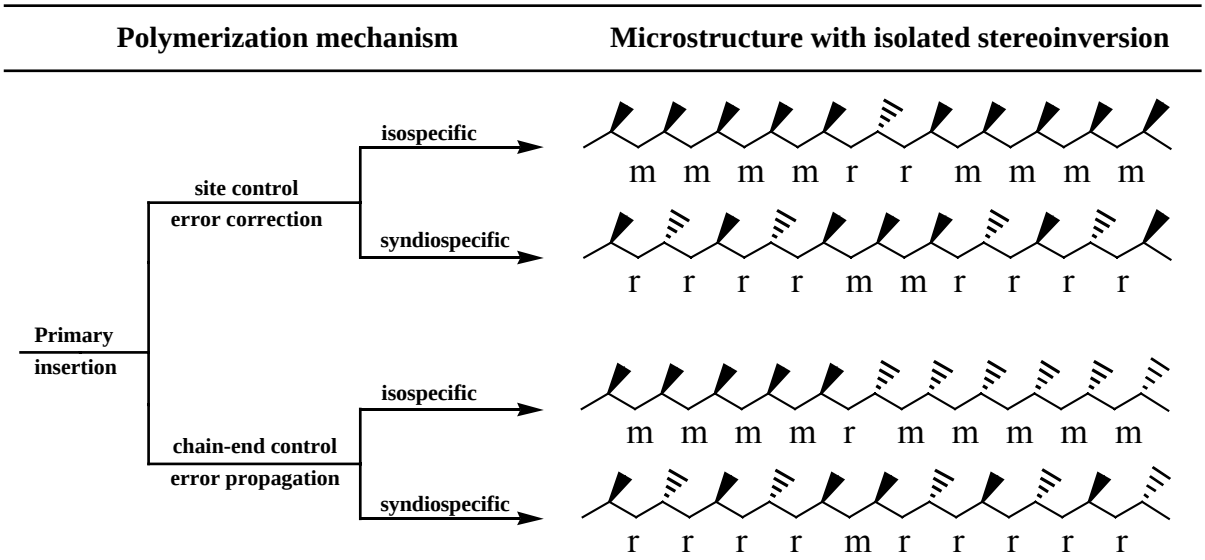


Figure 4.2. Schematic representation of the origin of $\Delta\Delta E^{\ddagger}$ in (*R*,*R*)-C$_2$H$_4$(1-Ind)$_2$ZrCl$_2$.[2,15]

Chain-end control is less effective than site control since the differences in activation energy between the insertion of the two enatiofaces by chain-end control are around 2 kcal/mol.[2,13,16,17] Isospecific chain end control is effective only at low temperatures but the resulting polymers show low stereoregularity.

According to proposed mechanisms of stereocontrol in primary 1-olefin polymerization (Scheme 4.2), when the enantiomorphic site control is used, stereoerrors do not propagate and can be fixed since the metal active site still has the same stereogenicity. In contrast, when the chain-end control is operative, the stereoerror propagates itself until another error occurs since the stereogenicity of the last formed stereogenic carbon is changed whenever a wrong enantioface is inserted.[2,15]

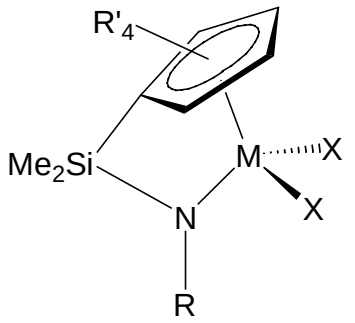
Scheme 4.2. Mechanisms of Stereocontrol in Primary 1-Olefin Polyinsertion.[2]



In order to generate single handed helical polymers, we need to synthesize chiral d^0 metal catalysts for controlling stereoselectivity of poly(α-olefin)s. The two main reasons are the site control from chiral coordination site could be more effective than the chain end control and the propagation by stereoerrors can lead to an opposite single handed helical conformation in the chain end control.

Among the group IV metal complexes of titanium, zirconium, and hafnium, the zirconium catalysts have received the most interest both academically and industrially since the titanium catalysts are unstable at conventional polymerization temperatures (~70ºC) and the hafnium systems are too expensive, since zirconium (0.022% in the lithosphere) is less abundant than titanium (0.63% in the lithosphere) but roughly 40 times as abundant as hafnium (0.0053% in the lithosphere).[9,18] Generally many kinds of zirconocene catalysts have been used for precise stereoregular control of polypropene,[1,2,7] but there are few catalysts for polymerization of more sterically encumbered α-olefins such as 1-hexene, 1-octene, styrene, vinylcycohexane.

For this research, we need new catalysts for polymerization of more sterically encumbered α-olefins to prevent racemization through main chain bond rotation of single handed helical poly(α-olefin)s. There are a few catalysts capable of polymerization of more sterically bulky α-olefins in non-metallocene catalysts. One example is the monocyclopentadienyl-amido (CpA) group IV catalysts developed by Dow and Exxon (Figure 4.3).[3] One of the important features of these catalysts is the open nature



R = alkyl, aryl
M = Ti, Zr
X = Cl, Me

Figure 4.3. The CpA Catalyst.

of the catalyst active site which allows them to incorporate other bulky olefins into polyethylene such as 1-hexene, 1-octene, styrene, and norbornene.[19-37] Additionally, when compared to bis-cyclopentadienyl metallocenes, CpA catalysts have increased stability toward MAO, are remarkably stable up to reaction temperatures of 160°C, and give generally higher molecular weight polymers.[38]

For this research one of the most interesting leads could be the half-sandwich zirconium amidinate catalysts, synthesized by carbodiimide insertion into a Zr-CH_3 bond of $CpZr(CH_3)_3$ ($Cp = \eta^5$-C_5H_5), developed by Sita's group (Figure 4.4).[5,6,39] These achiral, Cs-symmetric precatalysts can polymerize vinylcyclohexanes by the chain end control, and presumably more sterically encumbered monomers, and the resulting polymers are highly isotactic polyvinylcyclohexanes. These polymerizations provided narrow polydispersities (Mw/Mn = 1.04-1.10).

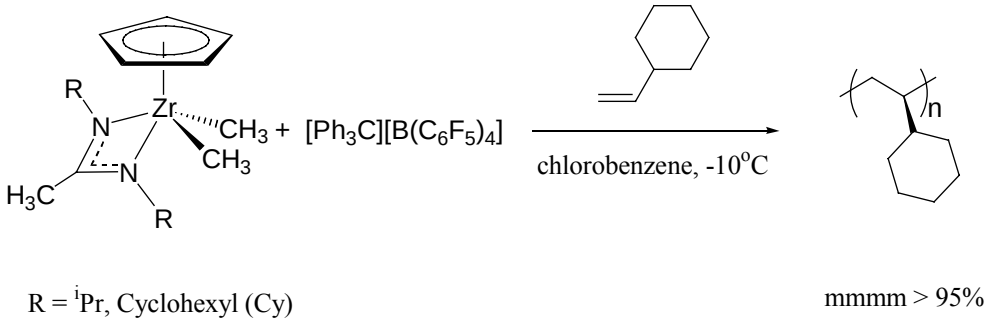
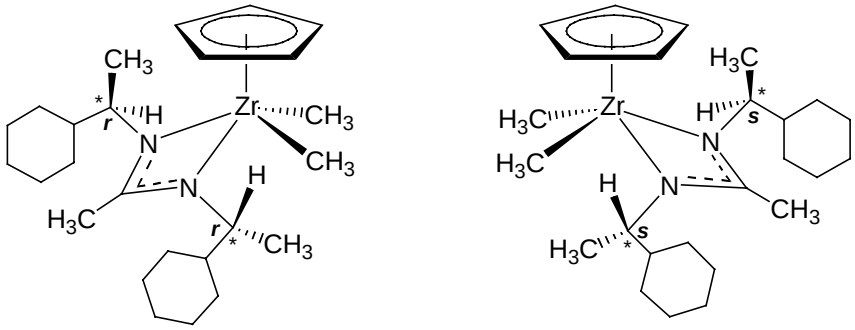
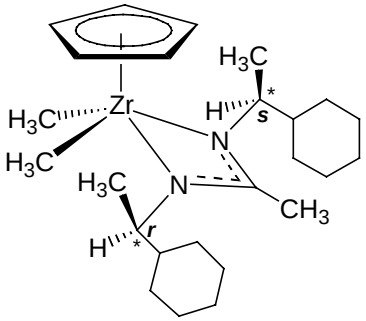


Figure 4.4. Isospecific living polymerization of vinylcyclohexane with achiral zirconium amidinate catalysts.

These kinds of zirconium amidinate catalysts will be our starting point to synthesize new chiral zirconium catalysts since bulky α-olefins can be polymerized for generating single handed helical poly(α-olefin)s. If amidinate ligands have two chirality centers, only three, not four, stereoisomeric complexes are possible (Figure 4.5). Zirconium (R,R)-amidinate complex and zirconium (S,S)-amidinate complex are enantiomers of each other and chiral complexes. Zirconium (R,S)-amidinate complex is achiral since the structure has a superimposable mirror image.



Chiral zirconium amidinate complex



Achiral zirconium amidinate complex

Figure 4.5. Three possible stereoisometic zirconium amidinate complexes.

For helix sense selective α-olefin polymerization bulky α-olefins are required, since bulky side groups can lead to high helix inversion barriers and prevent racemization through main-chain bond rotation. It is well known that highly isotactic and syndiotactic polypropylenes have a helical conformation and exist as a racemic mixture in the solid state,[40-45] but there are only a few examples for stereoregular poly(α-olefins) with bulky side chains.

According to the X-ray studies of oriented fibers of the isotatic polyvinylcyclohexanes, the polymer chains have a four-fold helical conformation and are a racemic mixture in solid state (Figure 4.6).[46-48] Because of its known high tacticity, vinylcyclohexane will be our starting monomer for this research.

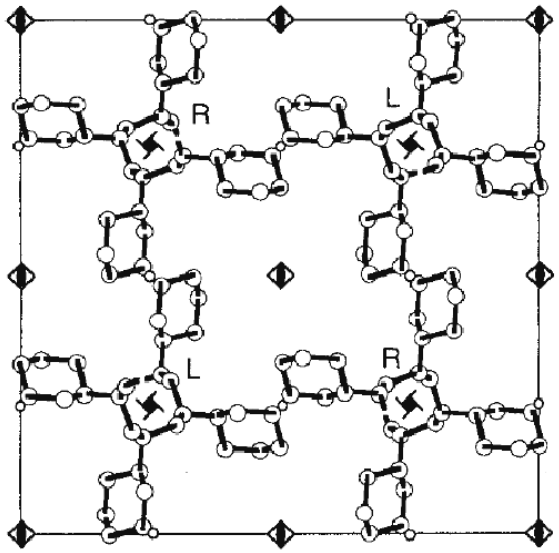
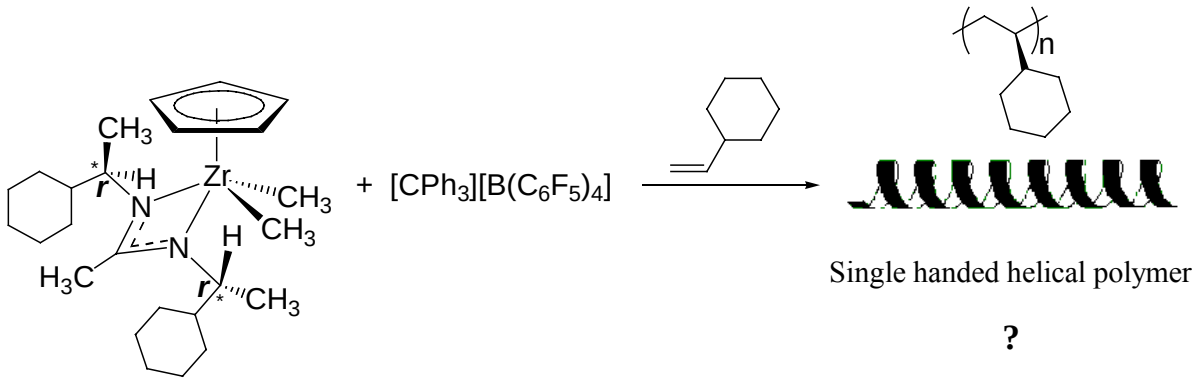


Figure 4.6. Packing of iPVCH chains of 4/1 helical conformation in the unit cell.[47]



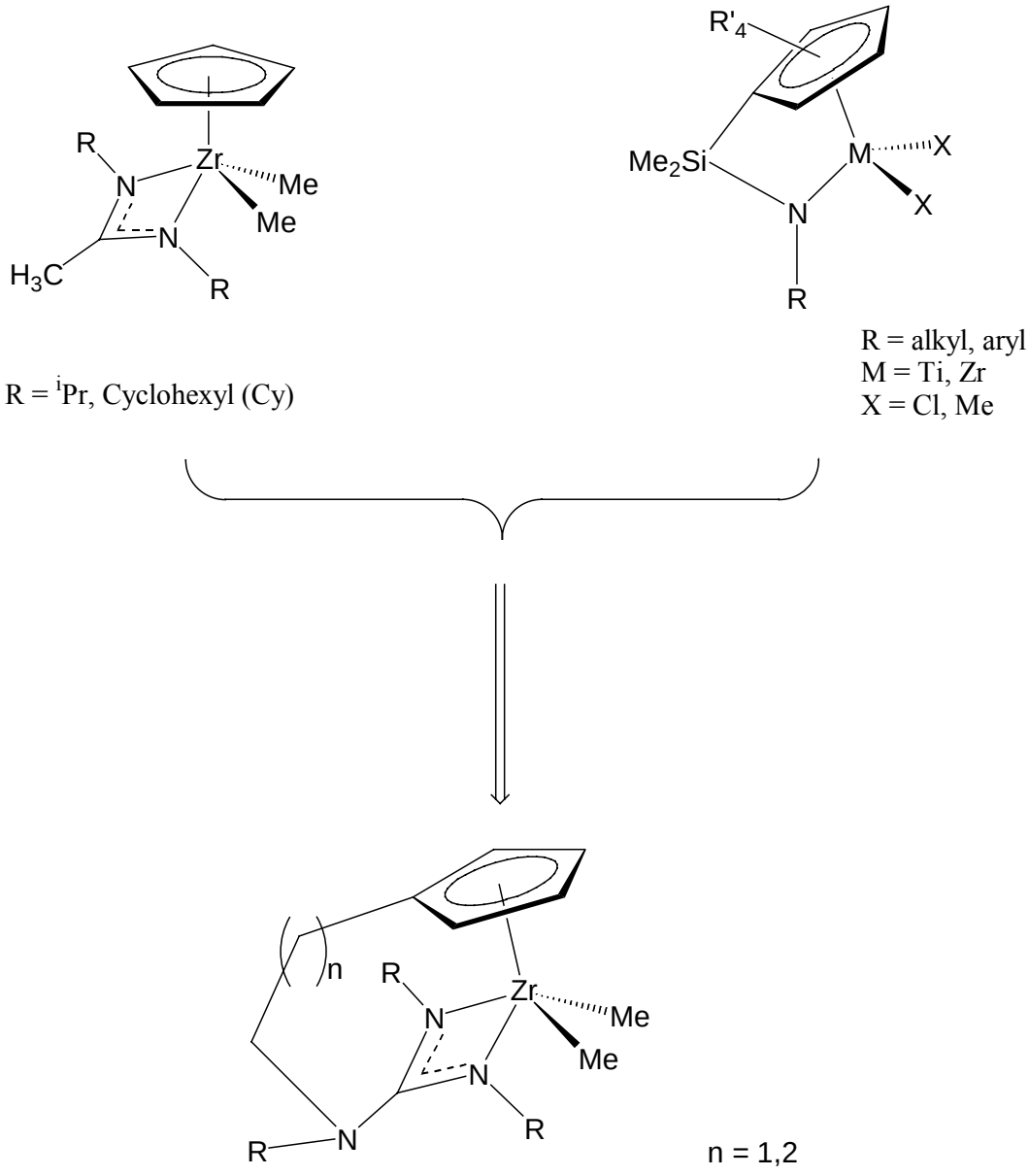
Scheme 4.3. Asymmetric polymerization of α-olefins by using chiral catalysts.

In this research, we want to synthesize these kinds of new chiral zirconium complexes and to determine whether this catalyst system can polymerize bulky α-olefins and control stereoregularity and helix sense selectivity of the polymer (Scheme 4.3).

Furthermore, for generating single handed helical poly(α-olefin)s we want to synthesize new chiral zirconium catalysts which have a more open nature of the catalyst active site to allow for the polymerization of bulky α-olefins and improve the stability under polymerization reaction conditions. As previously discussed, there are two good candidate catalysts. One is monocyclopentadienyl-amido (CpA) catalysts[19-37] and the other is half-sandwich zirconium amidinate catalysts.[39] We want to hybridize the interesting features of both of these catalysts for this research.

In order to combine all of the salient features of both of these catalysts, the open nature of catalytic active site, increased stability toward MAO and high polymerization temperature of monocyclopentadienyl-amido (CpA) catalysts and isospecific living

polymerization of bulky α-olefins of half-sandwich zirconium amidinate catalysts, into a single catalyst, which would have the open nature and improve configurational stability and polymerize more bulky α-olefins, we think this could be accomplished by bridging between cyclopentadienyl and amidinate ligands (Scheme 4.4).



Scheme 4.4. The hybridized zirconium catalysts.

One of the ultimate goals of this work is to synthesize chiral zirconium complexes for asymmetric coordination-insertion polymerization of α-olefins.

4,2 Results and discussion

4.2.1. Synthesis of a new chiral half-sandwich zirconium amidinate complex, (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl)

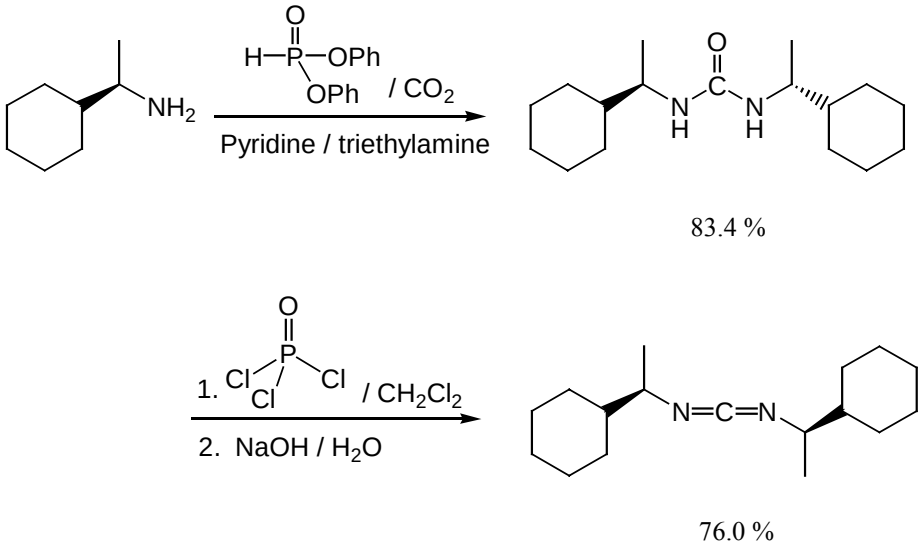
As previously discussed, the half-sandwich zirconium amidinate catalysts were synthesized by carbodiimide insertion into a Zr-CH_3 bond of $CpZr(CH_3)_3$ (Cp = η^5-C_5H_5).[39] We need appropriate chiral carbodiimides in order to synthesize the chiral half-sandwich zirconium amidinate complexes in Figure 4.5. The chiral carbodiimides should have two equal alkyl groups with the same chiral center.

In order to synthesize the chiral carbodiimides, we followed the published procedures discovered by Iguchi's group.[49] N,N'-bis[(R)-(-)-1-cyclohexylethyl]urea (83.4%) was prepared by carbonylation of (R)-(-)-1-cyclohexylethyl amine and carbon dioxide by means of diphenyl phosphites in the presence of tertiary amines (Scheme 4.5).

N,N'-bis[(R)-(-)-1-cyclohexylethyl]carbodiimide (76.0%) was synthesized by the method of Nobou involving dehydration of the urea by its addition to phosphorus oxychloride in non-basic organic solvents and deprotonation of the intermediates with aqueous sodium hydroxide solution (Scheme 4.5).[50]

To synthesize the new chiral half-sandwich zirconium amidinate complex, we followed literature procedures involving methylation of $CpZrCl_3$ with methyl lithium, followed by addition of N,N'-bis[(R)-(-)-1-cyclohexylethyl]carbodiimide which led to (η^5-

$C_5H_5)ZrCl_2[N(R)C(Me)N(R)]$ (R = (R)-1-cyclohexylethyl) (45%) which was characterized by single-crystal X-ray diffraction (Figure 4.7).



Scheme 4.5. The synthesis of N,N'-bis[(1R)-(-)-1-cyclohexylethyl]carbodiimide.

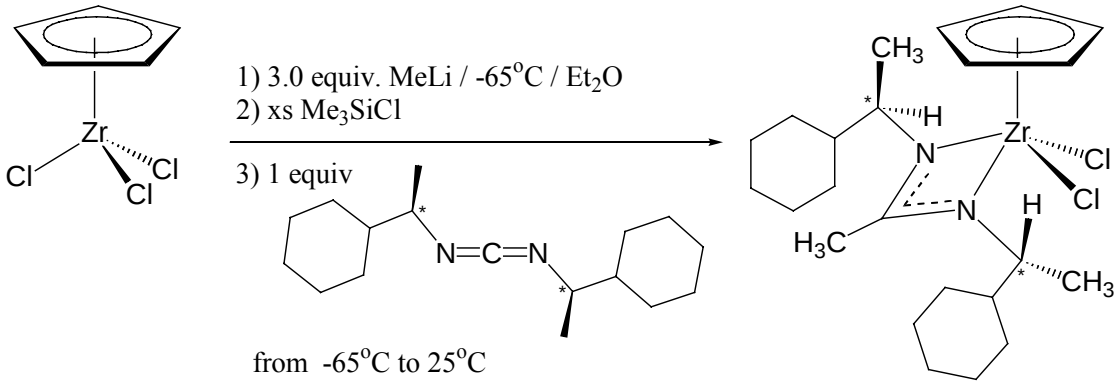


Figure 4.7. Synthesis of a new chiral half-sandwich zirconium amidinate complex, (η^5-$C_5H_5)ZrCl_2[N(R)C(Me)N(R)]$ (R = (R)-1-cyclohexylethyl).

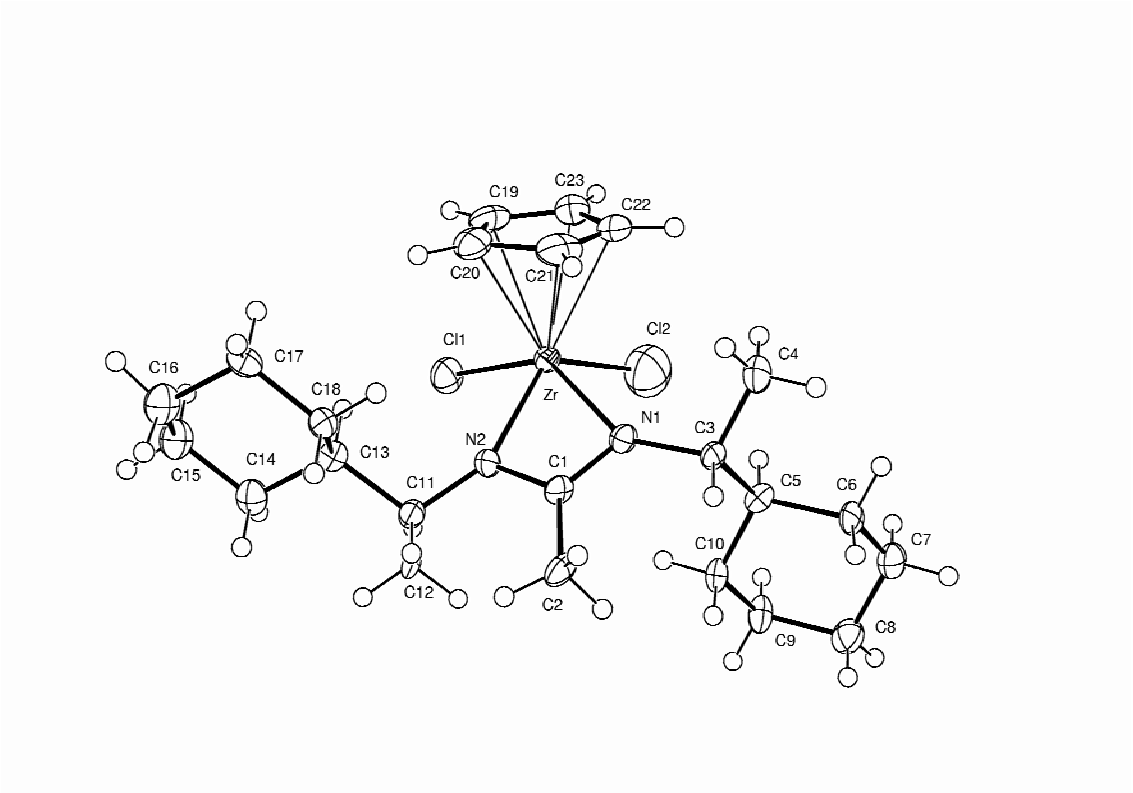


Figure 4.8. The ORTEP diagram of the (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl).

Table 4.1. Crystallographic data for (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl).

Selected Bond Lengths (Å)				
Zr-Cl(1) 2.453(2)	Zr-Cl(2) 2.413(4)	Zr-N(1) 2.252(5)	Zr-N(2) 2.202(6)	
Zr-C(19) 2.496(8)	Zr-C(20) 2.519(9)	Zr-C(21) 2.532(9)	Zr-C(22) 2.535(9)	
Zr-C(23) 2.519(8)	N(1)-C(1) 1.332(10)	N(2)-C(1) 1.364(9)	C(1)-C(2) 1.484(11)	
Selected Bond Angles (deg)				
Cl(1)-Zr-Cl(2) 90.27(10)	N(1)-Zr-N(2) 59.8(2)			
N(1)-C(1)-N(2) 110.8(6)	N(1)-C(1)-N(2) 110.8(6)			

A dimethyl derivative was expected, but X-ray crystallographic analysis of the complex revealed it as the dichloride derivative, (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl). The compound is noncentrosymmetric in the solid state with no unusual bond lengths or coordination geometry being present (Table 4.1). According to the crystal structure in Figure 4.8, the amidinate ligand has two chirality centers which have the R configuration and the complex is homochiral.

In order to synthesize the (η^5-C_5H_5)$Zr(CH_3)_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl), two different methylating reagents were used but neither lead to the methylated complex (Figure 4.9). This complex, (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl), may not be stable with methylating reagents since generally ligand redistribution and decomposition of complexes can happen during the methylation if complexes have low configurational stability.[51]

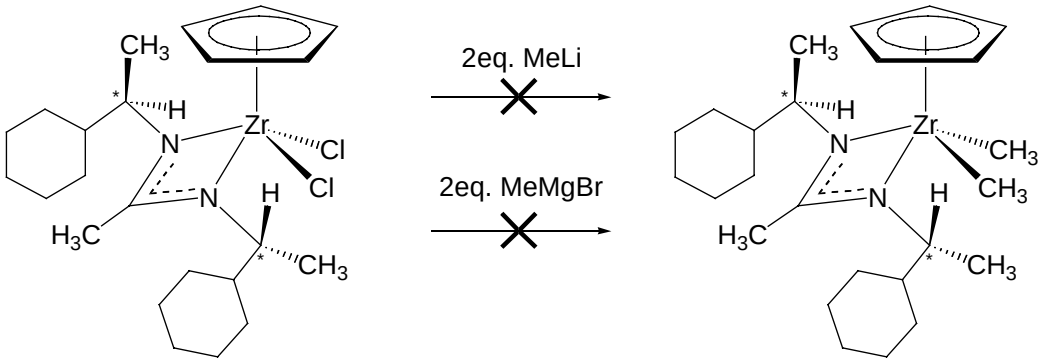


Figure 4.9. The reaction of the (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl) with methylating regents.

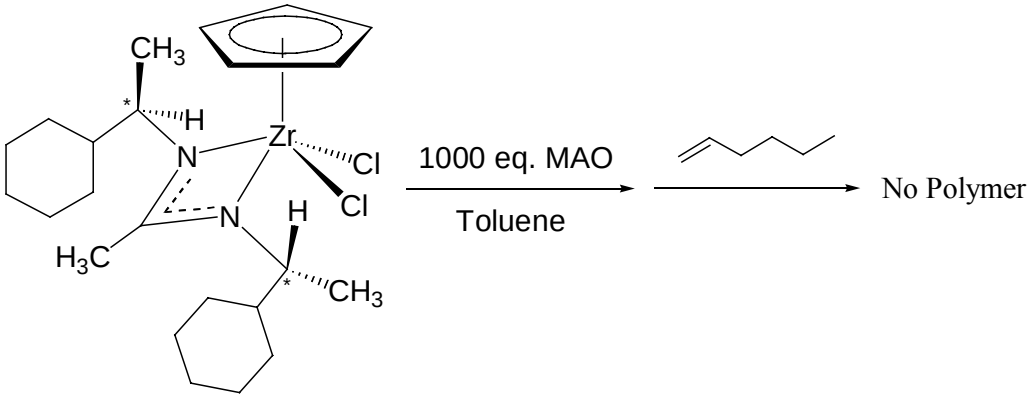


Figure 4.10. The polymerization of 1-hexene by using (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl) and MAO.

Generally catalyst precursors such as metallocene dichloride complexes for α-olefin polymerizations can be activated by methylalumoxane (MAO), which often provides maximum activity.[52-58] In order to activate the chiral complex (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl), the MAO cocatalyst was used for the polymerization of 1-hexene (Figure 4.10). Unfortunately, this catalytic system did not lead to the formation of any polymers.

4.2.2. Synthesis of dianionic C_2H_2–bridged Cp/guanidinate ligand for a CH_2CH_2-bridged Cp/guanidinate zirconium complex ($CpCH_2CH_2NCH_3C(=NR)NR)ZrCl_2$ (R = (R)-1-cyclohexylethyl)

As previously discussed in scheme 4.4, in order to bridge the cyclopentadienyl ligand and amidinate ligand, a synthetic route was devised to synthesize appropriate guanidinate-linked cyclopentadienyl ligands.

In order to synthesize dianionic C_2H_2–bridged Cp/guanidinate ligand $[CpCH_2CH_2NRC(=NR)NR]^{2-}$ (R = (R)-1-cyclohexylethyl) we modified a published method involving a nucleophilic addition of the lithium amide complex $[Li(TACN\text{-}iPr_2)]_2$ to spiro-[2.4]hepta-4,6-diene leads $Li[(C_5H_4)CH_2CH_2(TACN\text{-}iPr_2)]$ ($TACN\text{-}iPr_2$ = 4,7-diisopropyl-1,4,7-triaza-1-cyclononyl) (Figure 4.11).[59]

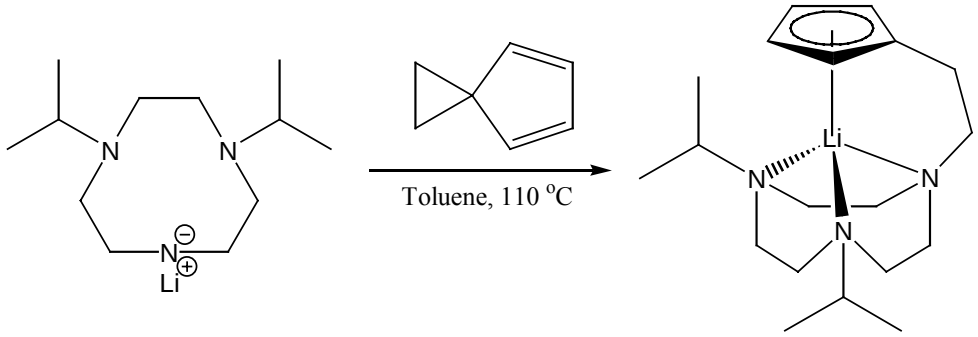
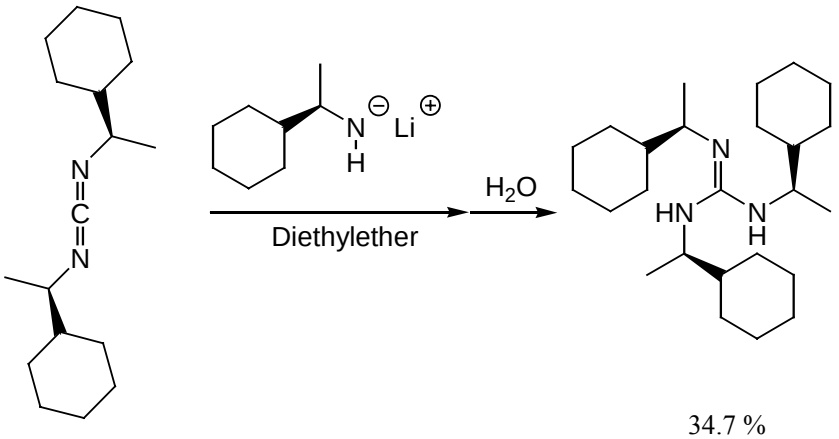


Figure 4.11. Lithium-amide-mediated opening of the cyclopropane ring in spiro[2.4]hepta-4,6-diene.[59]



34.7 %

$[\alpha]^{20}_{365}$ = -134.28° (0.2 w/v% in toluene)

Figure 4.12. The synthesis of chiral N,N',N''-tris[(1R)-(-)-1-cyclohexylethyl]guanidine.

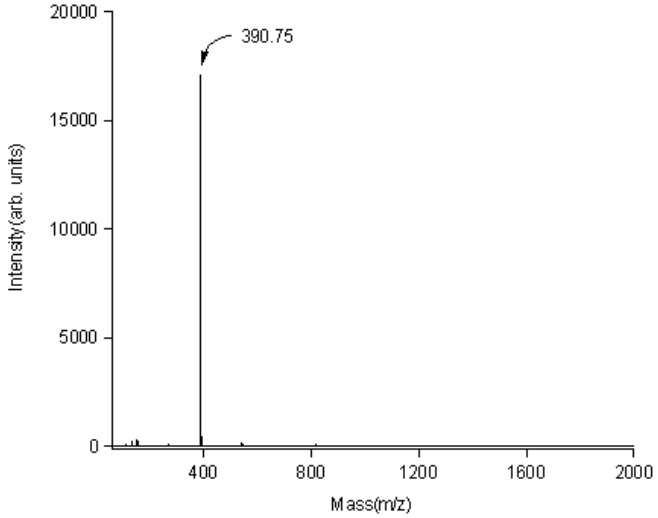


Figure 4.13. MALDI-MS of chiral N,N',N''-tris[(1R)-(-)-1-cyclohexylethyl]guanidine.

First, we needed to synthesize the lithum guanidinate Li[RNC(=NR)NHR] (R = (R)-1-cyclohexylethyl) to be used as a nucleophile to open the cyclopropane ring in spiro[2.4]hepta-4,6-diene. The new chiral N,N',N''-tris[(1R)-(-)-1-cyclohexylethyl]guanidine (34.7%) was synthesized by nucleophilic addition of lithium (1R)-(-)-1-cyclohexylethylamide to N,N'-bis[(R)-(-)-1-cyclohexylethyl]carbodiimide and has optical activity ($[\alpha]^{20}_{365}$ = -134.28º (0.2 w/v% in toluene)) (Figure 4.12).

The pure guanidine was successfully prepared and confirmed by MALDI-MS. A single MS peak at *m/z* = 390.75 was observed (Figure 4.13) and corresponded well to the molecular weight (389.67 g/mol) of N,N',N''-tris[(1R)-(-)-1-cyclohexylethyl]guanidine.

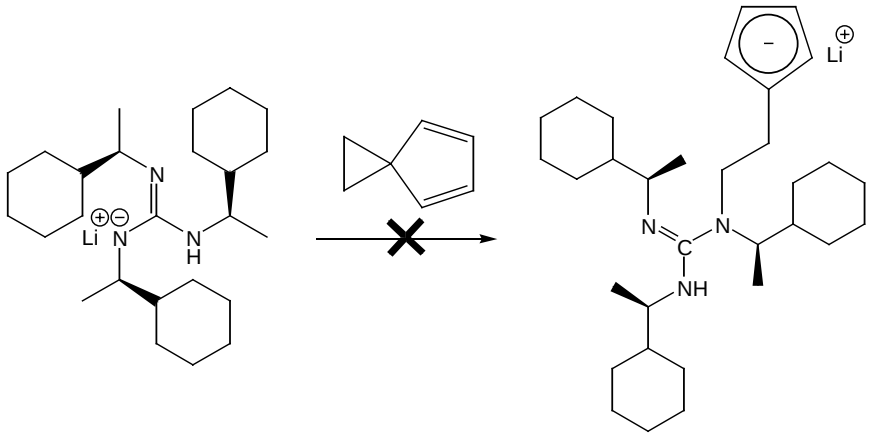


Figure 4.14. The reaction of spiro[2.4]hepta-4,6-diene and lithum guanidinate Li[RNC(=NR)NHR] (R = (R)-1-cyclohexylethyl).

In order to synthesize Li[$CpCH_2CH_2NRC$(=NR)NHR] (R = (R)-1-cyclohexylethyl), the reaction of spiro[2.4]hepta-4,6-diene and lithum guanidinate Li[RNC(=NR)NHR] (R = (R)-1-cyclohexylethyl) was tried under several different conditions (Figure 4.14).

Unfortunately the desired product was not synthesized. It appears the lithium guanidinate is too weak a nucleophile because of its resonance structures.

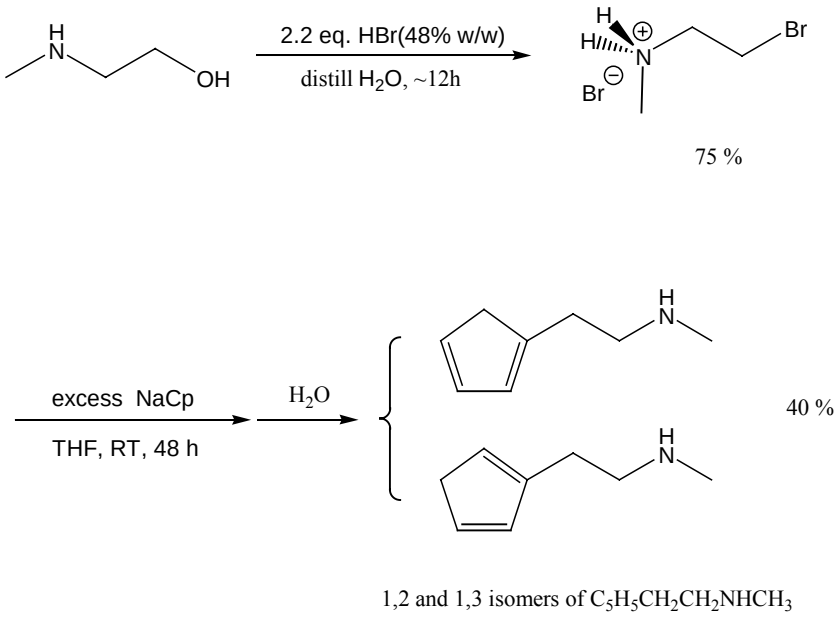
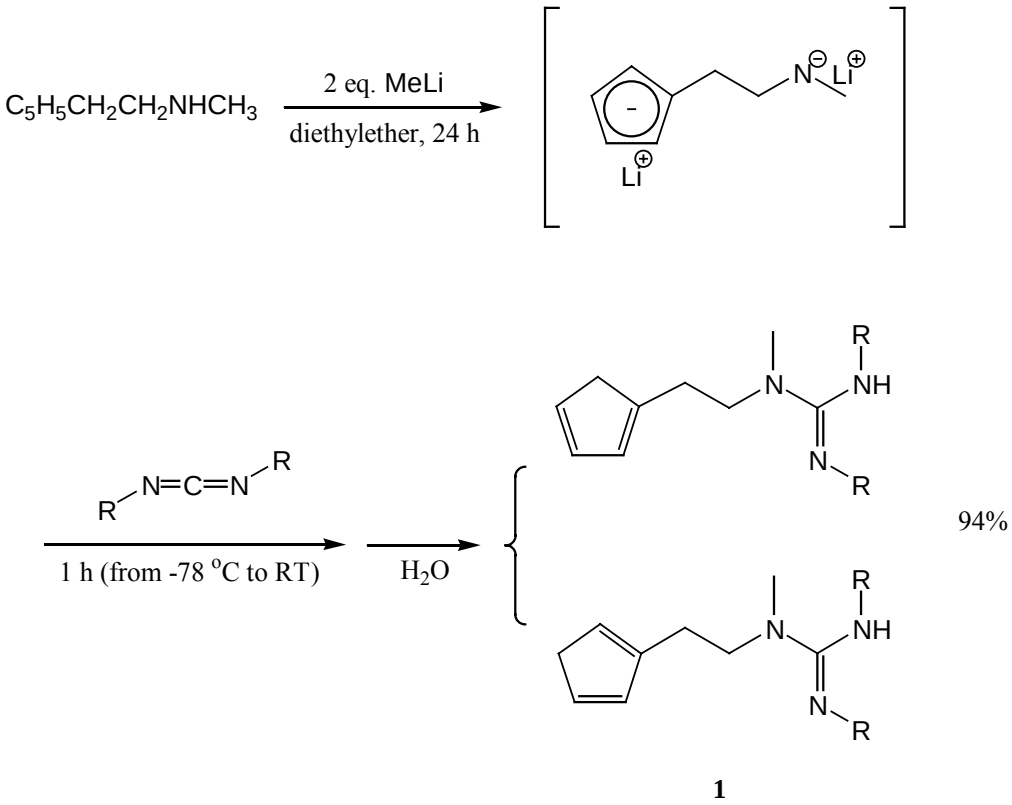


Figure 4.15. The synthesis of $C_5H_5CH_2CH_2N(H)CH_3$.

$Li_2[C_5H_4CH_2CH_2NCH_3]$ and N,N'-bis[(R)-(-)-1-cyclohexylethyl]carbodiimide can be used as starting materials for synthesis of $C_5H_5CH_2CH_2(CH_3)NC(=NR)NHR$ (R = (R)-1-cyclohexylethyl), **1.** (It is known from previous research that nucleophilic addition of lithium amide to carbodiimide can lead to guanidines.)

The synthesis of $Li_2[C_5H_4CH_2CH_2NCH_3]$, was carried out according to published procedures.[60-63] $C_5H_5CH_2CH_2N(H)CH_3$ (40%) was synthesized by nucleophilic substitution of excess sodium cyclopentadienide and $BrCH_2CH_2N(H)CH_3 \cdot HBr$ (75%), which in turn was synthesized by nucleophilic substitution of 2 equivalents of HBr and 2-(methylamino)ethanol

(Figure 4.15). The ^{1}H NMR spectrum showed the purified product to be a 1:1 mixture of two ring isomers with the alkyl group attached to the cyclopentadiene ring in the 1 and 2 positions. It was used immediately or stored under N_2 in the dark at -80°C since the instability of the cyclopentadiene ring of the product induces decomposition.[61,63]



1

Figure 4.16. The synthesis of $C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$ (R = (R)-1-cyclohexylethyl), **1**.

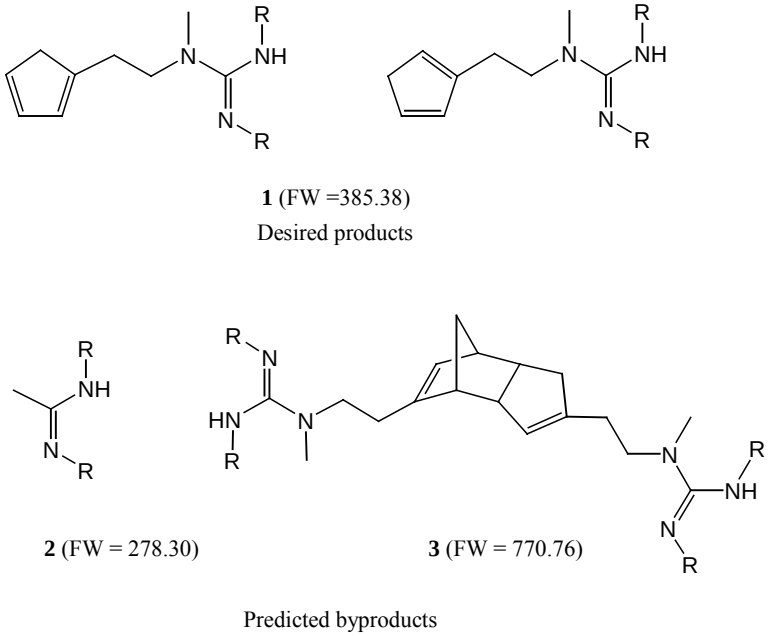


Figure 4.17. The predicted products from the synthesis of $C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$ (R = (R)-1-cyclohexylethyl), **1**.

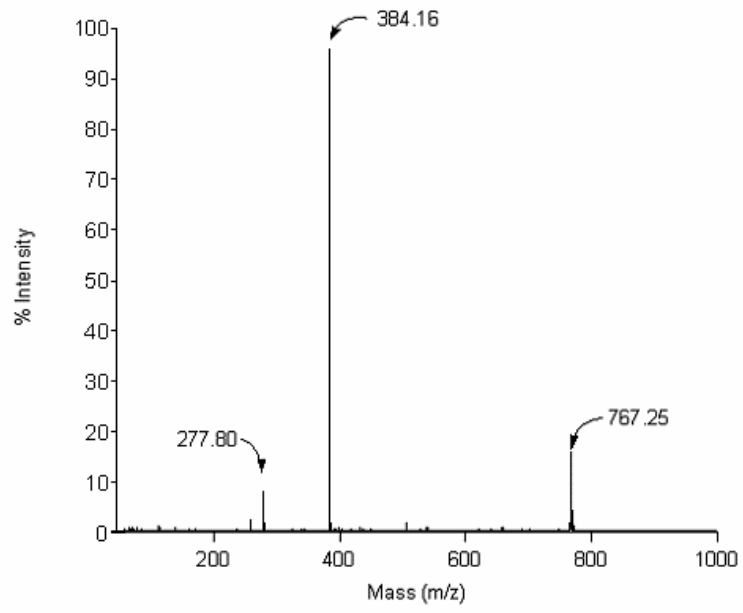


Figure 4.18. MALDI-MS of the crude product **1** in Figure 4.16.

$C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$ (R = (R)-1-cyclohexylethyl), **1**, (94%) was synthesized by nucleophilic addition of N,N'-bis[(R)-(-)-1-cyclohexylethyl]carbodiimide and the intermediate $Li_2[C_5H_4CH_2CH_2NCH_3]$ which can be formed by 2 equivalents of methyl lithium and $C_5H_5CH_2CH_2N(H)CH_3$ (Figure 4.16).

MALDI-MS was used in order to confirm whether the synthesis in Figure 4.16 lead to $C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$ (R = (R)-1-cyclohexylethyl), **1**. The major MS peak at *m/z* 384.16 in Figure 4.18 was observed and corresponded well to the molecular weight (385.38 g/mol) of the desired two isomers, **1**, in Figure 4.17. A MS peak at *m/z* 277.80 in Figure 4.18 was observed and corresponded well to the molecular weight (278.30 g/mol) of the amidine ($CH_3C(=NR)NHR$, R = (R)-1-cyclohexylethyl), **2**, which results from the reaction of residue methyl lithium and the carbodiimides.

We assume that a MS peak at *m/z* 767.25 in Figure 4.18 can be produced by decomposition of the dicyclopentadiene derivative, **3** (MW = 770.76 g/mol),and resulted from Diels-Alder reaction of cyclopentadiene rings of two equivalents of **1**. Care must be taken because these kinds of cyclopentadiene derivatives can easily be decomposed by oxygen and temperature.[60-63]

In order to synthesize a CH_2CH_2-bridged Cp/guanidinate zirconium complex, we used zirconium tetrachloride and the intermediate $Li_2[CpCH_2CH_2NCH_3C(=NR)NR]$ (R = (R)-1-cyclohexylethyl), formed by 2 equivalents of methyl lithium and $C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$ (R = (R)-1-cyclohexylethyl), **1**, (Figure 4.19).

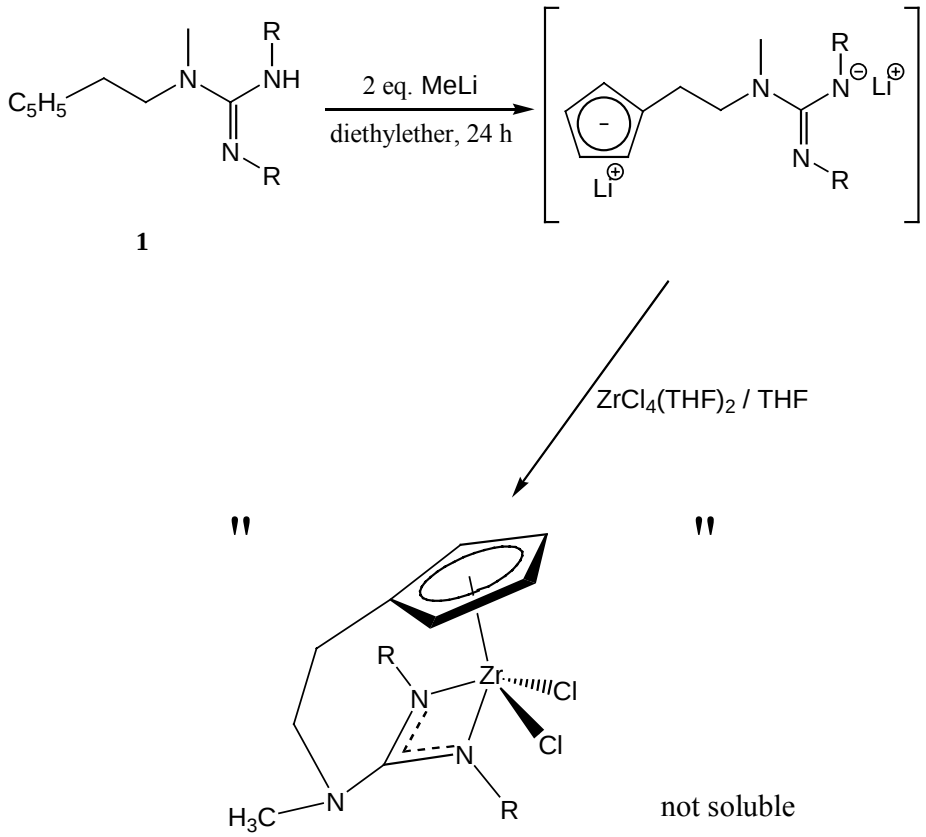


Figure 4.19. The synthesis of a CH_2CH_2-bridged Cp/guanidinate zirconium complex $(CpCH_2CH_2NCH_3C(=NR)NR)ZrCl_2$ (R = (R)-1-cyclohexylethyl).

Unfortunately the purified zirconium complex does not dissolve in any selected solvents (such as tetrahydrofuran, diethylether, chloroform, dichloromethane, toluene, benzene). It could be that the zirconium complex is a polymer with bridges between individual metal since the length of ligand with Cp ligand and guanidinate ligand is so short that both ligands could not coordinate a zirconium metal site.

4.3. Conclusions

A new chiral half-sandwich zirconium amidinate complex, (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl) was synthesized. In order to activate the chiral complex (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl), MAO cocatalyst was used for the polymerization of 1-hexene. Unfortunately, this catalytic system did not lead to the formation of any polymers.

We discovered a new synthetic method for new dianionic C_2H_2–bridged Cp/guanidinate ligands. $C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$ (R = (R)-1-cyclohexylethyl), **1**, was synthesized. Unfortunately zirconium tetrachloride and the intermediate Li_2[$CpCH_2CH_2NCH_3C(=NR)NR$] (R = (R)-1-cyclohexylethyl), with 2 equivalents of methyl lithium and $C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$ (R = (R)-1-cyclohexylethyl), **1,** did not lead to the desired CH_2CH_2-bridged Cp/guanidinate zirconium complex ($CpCH_2CH_2NCH_3C(=NR)NR)ZrCl_2$ (R = (R)-1-cyclohexylethyl).

4.4. Experimental Section

General procedures and characterizations

All synthetic manipulations were conducted in either a MBraun UNILab drybox under nitrogen atmosphrere or using a Schlenk line under an inert atmosphere of nitrogen. Dry and degassed solvents (MBraun solvent system) were used throughout.

^{1}H NMR spectra were obtained at 300 MHz and 400 MHz with Varian-Mercury NMR spectrometers. Chemical shift for ^{1}H NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane and are referenced to selected residual proton peaks of the solvent as follows: $CDCl_3$, 7.27, singlet; Acetone-d_6, 2.05 quintet.

Significant ^{1}H NMR data are tabulated in order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constant in Hertz, number of protons. $^{13}C\{^{1}H\}$ NMR proton decoupled NMR spectra were measured at 100 MHz on a Varian-Mercury spectrometer. Chemical shifts for $^{13}C\{^{1}H\}$ NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to selected residual peaks of the solvents as follows: $CDCl_3$, CD_2Cl_2. CD_2Cl_2 was stirred over CaH_2 overnight before being distillated and degassed.

Before sample analysis, solvents were removed with a rotary evaporator and under Schlenk line vacuum (approximately 60 mTorr). Toluene, Et_2O, methylene dichloride, and hexane used for reactions with air and moisture sensitive materials were purified by passing through one column filled with activated A2 Alumina catalyst and one column filled with activated Q5 copper catalyst under nitrogen atmosphere (MBraun solvent system). Tetrahydrofuran (THF) was distilled from sodium/benzophenone (with a few milliliters of triglyme being added to the pot in the case of pentane) and degassed.

All infrared spectra (cm^{-1}) were recorded on NaCl plates and were acquired on a JASCO FT/IR-410 spectrometer. Wavenumbers in cm^{-1} are reported for characteristic peaks. Optical rotations were recorded on a JASCO P-1010 polarimeter at the room temperatures.

A Voyager DE-STR matrix-assisted laser desorption ionization mass spectrometer (MALDI-TOF) was used. A linear positive detection mode was used; each spectrum was collected by averaging 80 laser shots. The best detection was achieved at a 93% grid voltage of 20000 V and a 20-ns delay time. The MALDI matrix solution contained DHB, acetonitrile, and water.

Unless indicated, all materials were purchased from Aldrich Chemical Company or Strem Inc.

Experimental procedures and characterizations

N,N'-bis[(R)-(-)-1-cyclohexylethyl]urea.

A modification of the procedure used by Iguchi T. et al. was employed.[49] The solution of (R)-(-)-1-cyclohexylethylamine (10.0 g, 78.6 mmol) and diphenyl phosphite (20 mL, 103.9 mmol) was prepared in pyridine (85 mL) and triethylamine (15 mL). Carbon dioxide was passed through the mixture at 60 ºC for 4 hours. The resulting mixture was concentrated to a syrup under reduced pressure. The syrup was added dropwise with stirring in 250 ml of 10% aqueous ethanol and then the precipitate was collected by filtration. Recrystallization of the product from methylene dichloride gave 83.4% (9.19 g) of N,N'-bis[(1R)-(-)-1-cyclohexylethyl]urea. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.95 (d), 3.59 (q), 1.76 (br d), 1.67 (br d), 1.08 (d), 0.95 – 1.4 (br m).

N,N'-bis[(R)-(-)-1-phenylethyl]urea.

The same procedure for the preparation of N,N'-bis[(1R)-(-)-1-cyclohexylethyl]urea was employed. The quantities of reagents used were (R)-(-)-1-phenylethylamine (10.0 g, 82.5 mmol) and diphenyl phosphite (20 mL, 103.9 mmol). Yield: 9.5 g (35.4 mmol, 85.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30 - 7.20 (m, 6H, *m, p*-C_6H_5), 7.13 (m, 4H, *o*-C_6H_5), 4.76 (q, 2H), 4.57 (d, 2H), 1.40 (d, 6H)

N,N'-bis[(R)-(-)-1-cyclohexylethyl]carbodiimide.

Most carbodiimides were prepared similarly with a slight modification of literature procedures.[50] The solution of phosphorus oxychloride (9 mL, 96.56 mmol) was prepared in methylene chloride (40 mL). N,N'-bis[(1R)-(-)-1-cyclohexylethyl]urea (9.0 g, 32.09 mmol) was slowly added with stirring to the solution under nitrogen at 0 ºC for 1 hour. The resulting mixture was stirred at 0 ºC for 2 hours. After the mixture was stirred for 4 hours in an oil bath (40 ºC), the solution was cooled at room temperature. The solution was added dropwise with stirring in 250 mL of NaOH (10 % w/w) for 1 hours. After the solution was stirred at 35 °C in a water bath for 12 hours, the solution was cooled at room temperature. 50ml of methylene dichloride was added in the solution and then the organic layer was separated. The aqueous layer was extracted with methylene dichloride (2 × 100 mL) and the combined organic layers were dried on Na_2SO_4 and filtered. The solvents were removed in vacuum and 50 ml of pentane was added to the viscous, yellow oil to precipitate the urea and filtered. Distillation of the extracts from CaH_2 at 150-160°C and 0.05 Torr afforded carbodiimide as a clear, colorless liquid. Yield: 6.4 g(24.4 mmol, 76.0%); IR: 2121 (s, N=C=N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.21 (t), 1.6 – 1.85 (br m), 1.2 (d), 0.9 – 1.3 (br m).

N,N'-bis[(R)-(-)-1-phenylethyl]carbodiimide.

The same procedure for the preparation of N,N'-bis[(R)-(-)-1-cyclohexylethyl]carbodiimide was employed. The quantities of reagents used were 9.0 g N,N'-bis[(R)-(-)-1-phenylethyl]urea (33.5 mmol), phosphorus oxychloride (9 mL, 96.56 mmol), 250 mL of NaOH (10 % w/w). Distillation: 150-160°C, 0.05 Torr. Yield: 6.7 g

(26.8 mmol, 80%); IR: 2115 (s, N=C=N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.4 – 7.2 (m, 10H), 4.59 (q, 2H), 1.49 (d, 6H).

N,N',N''-tris[(R)-(-)-1-cyclohexylethyl]guanidine.

(R)-(-)-1-cyclohexylethylamine (1.4 g, 11.0 mmol) in 20 mL of Et_2O was cooled to –78°C and 11.2 mmol of MeLi in 10 mL of Et_2O was added via a cannula. The mixture was stirred for 2 h at room temperature. N,N'-bis[(R)-(-)-1-cyclohexylethyl]carbodiimide (2.8 g, 10.7 mmol) in 10 mL of Et_2O was added to the mixture via a cannula at –78°C. The mixture was allowed to warm up to 20° C within a time span of 1 h and then quenched with the addition of deionized water (10 ml). The organic layer was separated and then the volatiles removed in vacuum (0.05 Torr) for 2 days. A yellowish oil was chromatographed (silica, methanol) to give colorless oil. Yield: 1.45 g (3.7 mmol, 34.7%); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.14 (t, 4H), 1.50 (tt, 4H), 1.23 (m, 12H), 0.82 (t, 6H); IR: 3435 (s), 2922 (m), 2850(s), 1650(s), 1487(s), 1448(s), 1375 (m), 1238 (m), 1157 (m); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 151.25 (s), 53.73 (s), 44.39 (s), 29.98 (s), 29.58 (s), 26.95 (s), 26.73 (s), 18.75 (s); MALDI-MS: *m/z* = 390.75 (Calc'd MW = 389.67 g/mol).

Synthesis of (η^5-C_5H_5)$ZrCl_2$[N(R)C(Me)N(R)] (R = (R)-1-cyclohexylethyl).

According to the procedure used by Sita's group,[39] (η^5-C_5H_5)$ZrCl_3$ (0.50 g, 1.9 mmol) in 50 ml of Et_2O was cooled to –78° C and 6.0 mmol of MeLi in 25 mL of Et_2O was added via a cannula. The mixture was stirred for 1 h at –65° C and then quenched with the addition of an excess of trimethylsilylchloride (3 ml) added via a syringe. N,N'-bis[(1R)-(-)-1-cyclohexylethyl]carbodiimide (0.39 g, 1.5 mmol) in 25 ml of Et_2O was then added via a

cannula at –78° C and the mixture was allowed to warm up to –20° C within a time span of 90 min. The reaction flask was taken out of the cold bath, stirred for 30 min at room temperature, and then the volatiles were removed in vacuum. The resulting residue was extracted with pentane to provide a crude product from the pentane extracts that was recrystallized from pentane at –30° C to afford the product as a white crystalline solid (0.43 g, 45%) which was characterized by single-crystal x-ray diffraction.

Spiro[2,4]hepta-4,6-diene.

According to the published procedures,[59] cyclopentadiene (17.42 mL, 0.21 mol) was added dropwise over 1 h to a suspension of NaH (18.18 g of a 60% suspension in mineral oil, 0.45 mol) in THF(120 mL) at 0 °C. After stirring at room temperature for 20 min, the resulting pink solution was cooled to 0 °C, and 1,2-dichloroethane (13.78 mL, 0.17 mol) was added dropwise over 1 h. The reaction mixture was stirred at room temperature overnight. Wet THF was carefully added, at 0 °C, to destroy the residual NaH. Water(80 mL) and pentane (80 mL) were then added, and the phases were partitioned. The aqueous layer was washed with pentane (2 × 40 mL). The combined organic layers were washed with brine (100 mL), dried and filtered. The pentane was removed by distillation at atmospheric pressure, and the residue then fractionally distilled to afford Spiro[2,4]hepta-4,6-diene as a colorless liquid. Yield: 9.81 g (0.106 mol, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 4H, C*H2*C*H2*), 6.12-6.55 (stack, 4H, C*H*).

Synthesis of $BrCH_2CH_2N(H)CH_3 \cdot HBr$.

A 250 mL round-bottom flask was charged with a stirbar and 100 mL (0.883 mol) of HBr (48% w/w). The solution was cooled to 0 °C in a ice bath, and 35 mL (0.438 mol) of 2-(methylamino)ethanol was added dropwise with stirring. The resulting mixture was then attached to a distillation apparatus that had a 2 in, fractionating column built into the distillation head, and the solution was brought to reflux by heating in an oil bath. As the bath temperature neared 150 °C, the head temperature reached 100 °C and distillation of H_2O began. The distillation was allowed to continue slowly (9-11 h) until ~70 mL of distillate was collected. During this time, distillation was performed for ~1 h, and then the oil bath was turned down to the point that reflux continued but distillation ceased for 30 min. In our hands, the distillation/reflux process was repeated four times. When the solution no longer produced any distillate at a head temperature of 100 °C, the bath temperature was increased, the head temperature rose to ~123 °C, and distillation of crude HBr began. After the solution had cooled to 60 °C, it was slowly poured with stirring into a 500 mL beaker containing 300 mL of ice cold acetone, whereupon the desired white product precipitated from solution. This heterogeneous solution was capped and placed in the freezer (-30 °C) overnight. The white precipitate was then vacuum filtered through a 60 mL medium-porosity sintered glass funnel, washed three times with 100 mL aliquots of ice cold acetone, and dried in the funnel, yielding 72.0 g (75.3 %) of crude product. Recrystallization of the product from acetone gave 68.2 % (65.2 g) of $BrCH_2CH_2N(H)CH_3 \cdot HBr$. ^1H NMR (400 MHz, $CDCl_3$): δ 9.23 (br s, 2H, $[BrCH_2CH_2\mathit{N}(\mathit{H})_2CH_3]Br$), 3.84 (t, 2H, $[Br\mathit{CH_2}CH_2N(H)_2CH_3]Br$), 3.49 (t, 2H, $[BrCH_2\mathit{CH_2}N(H)_2CH_3]Br$), 2.83 (s, 3H, $[BrCH_2CH_2N(H)_2\mathit{CH_3}]Br$)

Synthesis of $C_5H_5CH_2CH_2N(H)CH_3$.

A 500 mL, dry Schlenk flask was charged with a stirbar and 18.0 g (0.082 mol) of $BrCH_2CH_2N(H)CH_3 \cdot HBr$. The flask was sealed with a rubber septum, and 250 mL of freshly distilled THF was added by cannula. The white heterogeneous solution was cooled to 0 °C in an ice bath, and sodium cyclopentadienide (100 mL, 0.2 mol) was added dropwise through a syringe. The milky, purple solution was covered to minimize exposure to light and allowed to slowly come to room temperature. After the solution was stirred for 48 h, it was noted that the solution had retained its milky purple appearance. Deoxygenated distilled water (100 mL) was added into the solution until it became homogeneous. The clear solution was diluted with 250 mL of light petroleum and the organic layer was separated The aqueous layer was extracted with 100 mL of light petroleum and the combined organic layers were washed with 100 mL of brine, dried on Na_2SO_4 and filtered. The solvents were removed in vacuum, the crude product (20.7 g) was vacuum transferred at 1 mm Hg and 25-30 ºC. Yield; 3.94 g (0.032 mol, 40%). ^{1}H NMR ($CDCl_3$) showed the purified product to be a 1:1 mixture of two ring isomers with the alkyl group attached to the cyclopentadiene ring in the 1 and 2 positions:[60] δ 6.45 (m, 3H, 2 × CH of C_5H_5 ring isomer 1, 1 × CH of C_5H_5), 6.28 (m, 1H, CH of C_5H_5 ring isomer 2), 6.23 (s, 1H, CH of C_5H_5 ring isomer 2), 6.09 (t, 1H, CH of C_5H_5 ring isomer 1), 2.98 (d, 2H, CH_2 of C_5H_5 ring isomer 1), 2.91 (d, 2H, CH_2 of C_5H_5 ring isomer 2), 2.78 (q, 2H, $C_5H_5CH_2CH_2N(H)CH_3$), 2.60 (m, 2H, $C_5H_5CH_2CH_2N(H)CH_3$), 2.45 (s, 3H, $C_5H_5CH_2CH_2N(H)CH_3$), 1.01 (b s, 2H, 2 × $C_5H_5CH_2CH_2N(H)CH_3$).

Synthesis of $C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$ (R = (R)-1-cyclohexylethyl), 1.

$C_5H_5CH_2CH_2N(H)CH_3$ (0.8 g, 6.5 mmol) in 20 mL of Et_2O was cooled to –78°C and 13.0 mmol of MeLi in 20 mL of Et_2O was added via a cannula. The mixture was stirred for 2 days at room temperature. N,N'-bis[(R)-(-)-1-cyclohexylethyl]carbodiimide (1.7 g, 6.47 mmol) in 10 mL of Et_2O was added to the mixture via a cannula at –78°C. The mixture was allowed to warm up to 20° C within a time span of 1 h and then quenched with the addition of deionized water (10 ml). The organic layer was separated and then the volatiles removed in vacuum (0.05 Torr) for 2 days to give an yellowish oil. Crude yield: 2.35 g (94%); MALDI-MS; *m/z* 384.16 ($C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$, R = (R)-1-cyclohexylethyl, **1**), 277.80 ($CH_3C(=NR)NHR$, R = (R)-1-cyclohexylethyl, **2**), 767.25 (decomposed material).

The synthesis of $CpCH_2CH_2NCH_3C(=NR)NR)ZrCl_2$ (R = (R)-1-cyclohexylethyl).

$C_5H_5CH_2CH_2N(CH_3)C(=NR)NHR$ (R = (R)-1-cyclohexylethyl), (1.0 g, 2.6 mmol) in 20 mL of Et_2O was cooled to –78°C and 6.5 mmol of MeLi in 10 mL of Et_2O was added via a cannula. The mixture was stirred for 2 h at room temperature. White solid was precipitated and the liquid was removed via a cannula. White solid was repeatedly washed by Et_2O and addition of THF (50 mL) gave white heterogeneous solution. The solution was added to $ZrCl_4(THF)_2$ (1.0 g, 2.65 mmol) in 100 mL of THF, cooled to -78°C. It became homogeneous and white solid was precipitated after the mixture was stirred for 2 h at room temperature. The volatiles were removed in vacuum. The resulting residue was extracted with pentane to provide a crude product from the pentane extracts. The crude product does not dissolve in any selected solvents (such as toluene, tetrahydrofuran, diethylether, benzene, chloroform, dichloromethane).

4.5. References

1. Alt, H. G.; Koppl, A., *Chem. Rev.* **2000,** 100, 1205-1221.
2. Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F., *Chem. Rev.* **2000,** 100, 1253-1346.
3. McKnight, A. L.; Waymouth, R. M., *Chem. Rev.* **1998,** 98, 2587-2598.
4. Ittel, S. D.; Johnson, L. K.; Brookhart, M., *Chem. Rev.* **2000,** 100 1169-1203.
5. Gibson, V. C.; Spitzmesser, S. K., *Chem. Rev.* **2003,** 103, 283-315.
6. Coates, G. W.; Hustad, P. D.; Reinartz, S., *Angew. Chem. Int. Ed.* **2002,** 41, 2236-2257.
7. Coates, G. W., *Chem. Rev.* **2000,** 100, 1223-1252.
8. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F., *Angew. Chem. Int. Ed.* **1999,** 38, 428-447.
9. Janiak, C., *Metallocenes*. Togni, A., Haltermann, R. L., Eds.; Wiley-VCH: New York, 1998; Vol. II, p 547-623.
10. Casey, C. P.; Lee, T.-Y.; Tunge, J. A.; II, D. W. C., *J. Am. Chem. Soc.* **2001,** 123, 10762-10763.
11. Angermund, K.; Fink, G.; Jensen, V. R.; Kleinschmidt, R., *Chem. Rev.* **2000,** 100, 1457-1470.
12. Rappe, A. K.; Skiff, W. M.; Casewit, C. J., *Chem. Rev.* **2000,** 100, 1435-1456.
13. Ewen, J. A., *J. Am. Chem. Soc.* **1984,** 106, 6355-6364.
14. Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D., *J. Am. Chem. Soc.* **1988,** 110, 6255-6256.
15. Resconi, L.; Piemontesi, F.; Camurati, I.; Sudmeijer, O.; Nifant'ev, I. E.; Ivchenko, P. V.; Kuz'mina, L. G., *J. Am. Chem. Soc.* **1998,** 120, 2308-2321.
16. Resconi, L.; Abis, L.; Franciscono, G., *Macromolecules* **1992,** 25, 6814-6817.
17. Erker, G.; Fritze, C., *Angew Chem., Int. Ed. Engl.* **1992,** 31, 199-202.

18. Wailes, P. C.; Courtts, R. S. P.; Weigold, H., *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*. Academic Press: New York, 1974; p 302.

19. Canich, J. C. M. Eur. Pat. Appl. 0 420 436 A1, 1991.

20. Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Y. Eur. Pat. Appl. 0 416 815 A2, 1991.

21. Pannell, R. B.; Canich, J. A. M.; Hlatky, G. G. PCT Int. Appl. WO 94/00500, 1994.

22. Canich, J. A. M. U.S. Patent. 5,096,867, 1992.

23. Brant, P.; Canich, J. A. M. PCT Int. Appl. WO 93/12151, 1993.

24. Brant, P.; Canich, J. A. M.; Merrill, N. A. PCT Int. Appl. WO 93/21242, 1993.

25. Brant, P.; Canich, J. A. M.; Dias, A. J.; Bamberger, R. L.; Licciardi, G. F.; Henrichs, P. M. PCT Intl. Appl. 94/07930, 1994.

26. Canich, J. A. M. PCT Int. Appl. WO 96/00244, 1996.

27. LaPointe, R. E.; Rosen, R. K.; Nickias, P. N. Eur. Pat. Appl. 0 495 375 A2, 1992.

28. LaPointe, R. E.; Stevens, J. C.; Nickias, P. N.; McAdon, M. H. Eur. Pat. Appl. 0 520 732 A1, 1992.

29. Lai, S. Y.; Wilson, J. R.; Knight, G. W.; Stevens, J. C. PCT Int. Appl. WO 93/08221, 1993.

30. Rosen, R. K.; Nickias, P. N.; Devore, D. D.; Stevens, J. C.; Timmers, F. J. U.S. Patent 5,374,696, 1994.

31. Devore, D. D.; Crawford, L. H.; Stevens, J. C.; Timmers, F. J.; Mussell, R. D.; Wilson, D. R.; Rosen, R. K. PCT Int. Appl. WO 95/00526, 1995.

32. Nickias, P. N.; McAdon, M. H.; Patton, J. T. PCT Int. Appl. WO 97/15583, 1997.

33. Harrington, B. A. PCT Int. Appl. WO 96/40806, 1996.

34. Harrington, B. A.; Hlatkey, G. G.; Canich, J. A. M.; Merrill, N. A. U.S. Patent. 5,635,573, 1997.

35. Devore, D. D. Eur. Pat. Appl. 0 514 828 A1, 1992.

36. Sernetz, F. G.; Muelhaupt, R.; Waymouth, R. M., *Macromol. Chem. Phys.* **1996,** 197, 1071-1083.

37. Xu, G., *Macromolecules* **1998,** 31, 2395-2402.

38. Stevens, J. C., *Stud. Surf. Sci. Catal.* **1996,** 101, 11-20.

39. Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R., *J. Am. Chem. Soc.* **2001,** 123, 6197-6198.

40. Brückner, S.; Meille, S. V., *Nature* **1989,** 340, 455-457.

41. Meille, S. V.; Ferro, D. R.; Bruckner, S.; Lovinger, A. J.; Paddenl, F. J., *Macromolecules* **1994,** 27, 2615-2622.

42. Hirosea, M.; Yamamotoa, T.; Naikib, M., *Computational and Theoretical Polymer Science* **2000,** 10 345–353.

43. Auriemma, F.; Rosa, C. D.; Boscato, T.; Corradini, P., *Macromolecules* **2001,** 34, 4815-4826.

44. Rosa, C. D.; Corradini, P., *Macromolecules* **1993,** 26, 5711-5718.

45. Lovinger, A. J.; Lotz, B.; Davis, D. D.; F. J. Padden, J., *Macromolecules* **1993,** 26, 3494-3503.

46. Natta, G.; Corradni, P.; Bassi, I. W., *Die Makromolekulare Chemie* **1959,** 33, 247-248.

47. Nishikawa, Y.; Murakami, S.; Kohjiya, S.; Kawaguchi, A., *Macromolecules* **1996,** 29, 5558-5566.

48. Rosa, C. D.; Borriello, A.; Corradini, P., *Macromolecules* **1996,** 29, 6323-6327.

49. Yamazaki, N.; Higashi, F.; Iguchi, T., *Tetrahedron Letters* **1974,** 13, 1191 - 1194,.

50. Nobuo, Y. J. Patent. JP10330344, 1998.

51. Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G., *Organometallics* **2001,** 20, 1808-1819.

52. Andresen, A.; Cordes, H.-G. t.; Herwig, J.; Kaminsky, W.; Merck, A.; Mottweiler, R.; Pein, J.; Sinn, H. g.; Vollmer, H.-J. g., *Angew. Chem., Int. Ed. Engl.* **1976,** 15, 630-632.

53. Sinn, H.; Kaminsky, W., *Advances in Organometallic Chemistry* **1980,** 18, 99-149.

54. Kaminsky, W.; Miri, M.; H., S.; Woldt, R., *Makromol. Chem. Rapid. Commun.* **1983,** 4, 417-421.

55. Barron, A. R., *Macromol. Symp.* **1995,** 97, 15-25.

56. Harlan, C.; Bott, S.; Barron, A. R., *J. Am. Chem. Soc.* **1995,** 117, 6465-6474.

57. Sinn, H., *Makromol. Chem. Macromol. Symp.* **1995,** 97, 27-52.

58. Barron, A. R., *J. Am. Chem. Soc.* **1993,** 115, 4971-4984.

59. Qian, B.; Henling, L. M.; Peters, J. C., *Organometallics* **2000,** 19, 2805-2808.

60. Schutte, E.; Weakley, T. J. R.; Tyler, D. R., *J. Am. Chem. Soc.* **2003,** 125, (34), 10319 - 10326.

61. Hughes, A. K.; Meetsma, A.; Teuben, J. H., *Organometallics* **1993,** 12, 1936-1945.

62. Hughes, A. K.; Marsh, S. M. B.; Howard, J. A. K.; Ford, P. S., *Journal of Organometallic Chemistry* **1997,** 528, 195-198.

63. Kaul, B. B.; Noll, S.; Renshaw, S.; Rakowski Dubois, M., *Organometallics* **1997,** 16, 1604-1611.