Chiral and Optically Active Polymers from Hydrocarbon Monomers

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der RWTH Aachen University zur Erlangung des akademischen Grades eines Dokors der Naturwissenschaften genehmigte Dissertation

vorgelegt von

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The work delineated here was carried out between August 2008 and June 2011 in the Laboratories of Prof. Dr. J. Okuda, at the Institut für Anorganische Chemie of the RWTH Aachen University, Germany.

List of Abbreviations.

[α]	specific optical activity
*t*Bu	*tert*-butyl
c	concentration
δ	chemical shift
d	doublet
DSC	differential scanning calorimetry
eq.	equivalent
EtOH	Ethanol
Et_2O	diethyl ether
GPC	gel permeation chromatography
HPLC	high-performance liquid chromatography
m	multiplet
M	metal
M_n	number average molecular mass
M_w	weight average molecular mass
MAO	methylaluminoxane
Me	methyl
MeOH	methanol
min	minute
NMR	nuclear magnetic resonance
p	*para*
PBD	polybutadiene
PD	polydispersity
Ph	phenyl
PS	polystyrene
ppm	parts per million
quart	quartet
s	singlet
solv	solvent
t	time
T	temperature
T_m	melting transition temperature
THF	tetrahydrofuran
wt%	weight percent

A. General Introduction

A helix is a chiral structure, and right- and left-handed helices are nonidentical mirror images of each other. The helix is the central structural motif in naturally occurring macromolecules, such as proteins and nucleic acids. Helices in such systems play important roles in realizing their elaborate functions in living systems involving molecular recognition, replication, and catalytic activity. Inspired by sophisticated biological helices, synthetic polymer scientists have been challenged to synthesize artificial helical polymers which can be adapted to ferroelectric liquid crystals or nonlinear optic materials and materials that allow sensing specific molecules as well as separation of enantiomers or asymmetric catalysis.[1-3]

The history of helical polymers dates back to 1930s, when Hanes proposed the helical structure of α-amylose.[4] Pauling proposed the α-helical structure for natural polypeptides.[5] Watson and Crick found the right-handed double-stranded helix for DNA in the early 1950s.[6] In 1955, Natta found that highly isotactic polypropylene adopts a helical conformation in the solid state but the polypropylene cannot maintain this conformation in solution.[7] Natta et al. also showed in crystalline isotactic polystyrene the molecular chains form three-fold helices.[8] Pino et al. investigated a helical structure for vinyl polymers with an excess helicity in solution, although the helical polyolefins are totally dynamic and composed of very short helical segments.[9]

In 1979 Okamoto et al. synthesized poly(triphenylmethyl methacrylate)s (PTrMA) that retain their helical conformations in solution at room temperature.[10] Green and co-workers found a dynamic helical polyisocyanate with chirality.[11-12] To mimic the ability of proteins, nucleic acids, and polysaccharides to fold into well-defined conformations, artificial molecules that adopts a secondary structure stabilized by noncovalent interactions were defined as foldamers by Gellman.[13] Moore et al., Hamilton, Lehn, and Hecht et al. designed and synthesized foldamers with a controlled helical sense.[14-17]

There are three types of helical polymers.

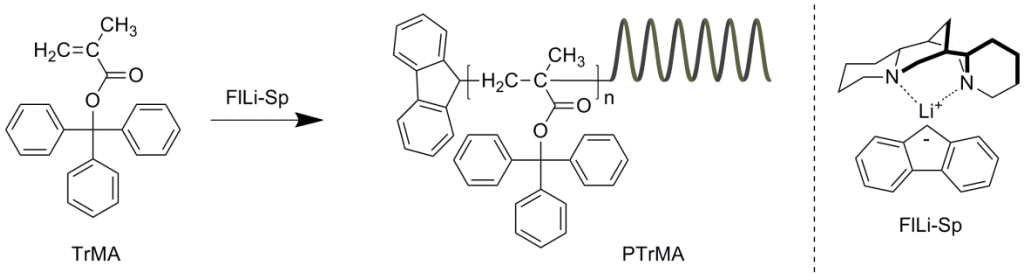
- **Static helical polymers** have high helix inversion barriers that stabilize helical conformation at room temperature.
- **dynamic helical polymers** have low helix inversion barriers, helix reversals can readily move along a polymer chain at room temperature.
- **Foldamers** retain their helical conformation under certain experimental conditions.[3]

In the following sections, important examples are given for these types of helical polymers.

A.1. Stable Helical Polymers

A.1.1. Polymethacrylates

Optically active polymers can be synthesized by polymerization of optically active monomers or the helix-sense-selective polymerization of achiral or prochiral monomers using chiral initiators or catalysts. Helical PTrMA was first synthesized by the helix-sense-selective polymerization of an achiral triphenyl methylmethacrylate **1** using a complex of 9-fluorenyllithium (FlLi) with (-)-sparteine.[18] Since a single-handed helical conformation is stabilized by steric repulsion of the bulky side groups, the optical activity disappears when the bulky triphenylmethyl side group is removed from the polymer chain.



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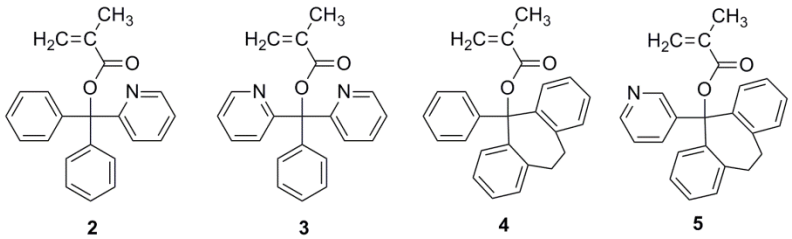
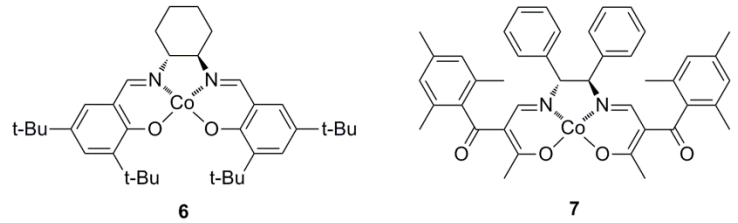
Since the discovery of the helix-sense-selective polymerization of TrMA, Okamoto et al. designed various other bulky monomers and investigated their helical structures, chiral recognition abilities and the mechanism of the helix-sense-selective polymerization (**2**, **3**, **4**, **5**). Inexpensive, experimentally simple free-radical polymerization can be used to produce helical polymethacrylates.[2] An almost perfect isotactic polymerization with an excess of one-handedness has been achieved by the free radical polymerization of **4** with 1,1'-azobisisobutyronitrile (AIBN) in the presence of chiral chain transfer agents or cobalt(II) complexes (**6**, **7**).[19]



2 **3** **4** **5**



6 **7**

Poly(2,7-di-n-pentyldibenzofulvene) has been synthesized by anionic polymerization using the complexes of FlLi with chiral (-)-sparteine. Poly(2,7-di-n-pentyldibenzofulvene) shows a significant CD signal in the solid state but hardly any chiroptical properties in solution.[20-21] Polymer **9** bearing a chiral terminal group has been prepared by anionic polymerization using potassium L-menthoxide as initiator. Polymer **9** shows CD bands in the absorption region of the fluorenyl units suggesting that the one-handed helical conformation is induced by the chiral terminal group.[22]

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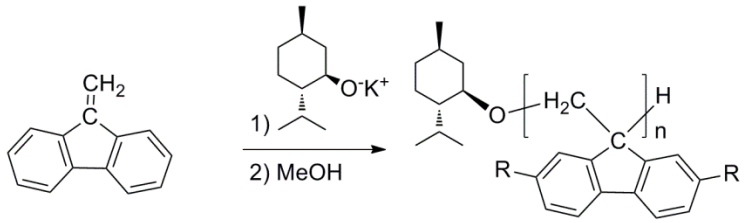

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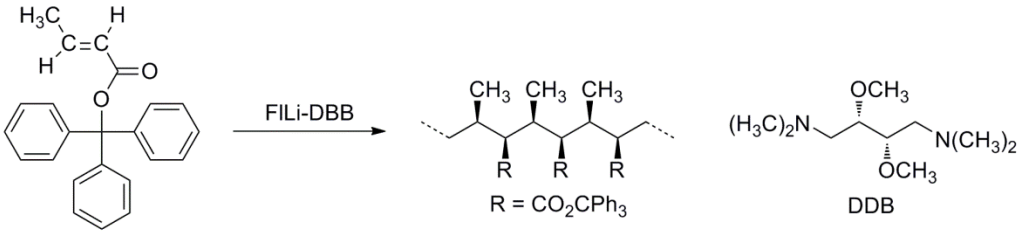
Triphenylmethyl crotonate has been polymerized with FlLi in the presence of (*S*,*S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB). Polymer **10** is optically active and highly threodiisotactic poly(triphenylmethyl crotonate). The optical rotation of polymer **10** decreases gradually and irreversibly at 60 °C due to the helix-helix transition of the main chain.[23]



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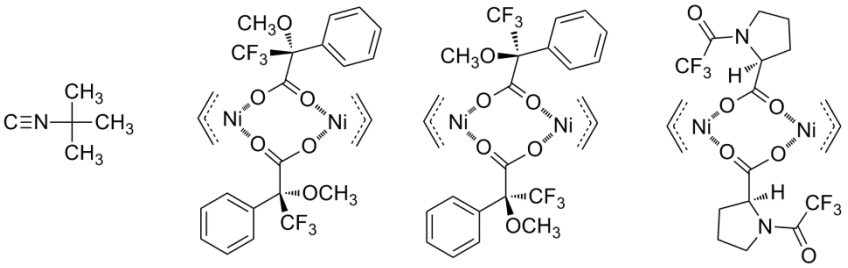
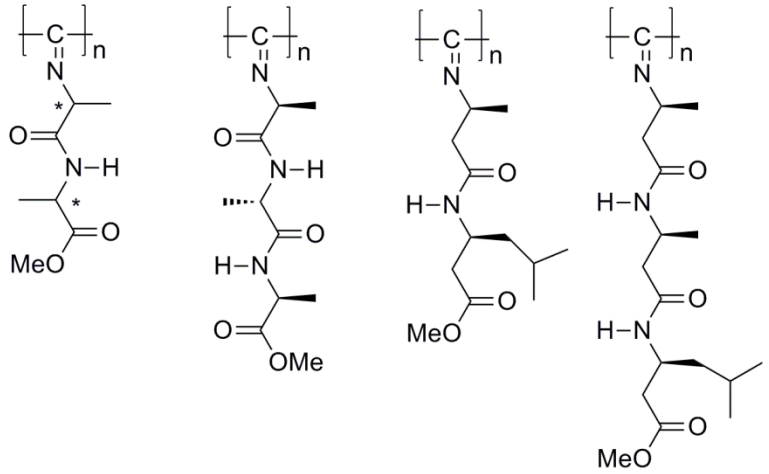
A.1.2. Polyisocyanides

Polyisocyanides have a 4/1-helical conformation in solution when a bulky side group is introduced.[24-27] Optically active polyisocyanides with an excess helicity are obtained by polymerizing bulky isocyanides using chiral matrix, chiral catalysts or optically active monomers.[28-29] Novak et al. reported on optically active polymers obtained by helix-sense-selective polymerization of *tert*-butyl isocyanide with optically active Ni catalysts **11-13**. Ni catalyst **13** converts *tert*-butylisocyanide to give an optically active polymer with 69 % ee.[30]



11 **12** **13**

Polyisocyanides with chiral peptide pendants **14** and **15** have been synthesized by polymerizing α-amino acid-bound isocyanide monomers using Ni(II) catalysts. They are stabilized by intramolecular hydrogen bonding networks formed between the peptide side chains. In contrast to denaturation of proteins, disruption of hydrogen bondings does not take place under strong acidic conditions demonstrating the robust helical scaffold assisted by hydrogen bonding arrays.[31-33] Helical structures of poly(isocyanate-β-peptide)s **16** and **17** are dynamic in nature. The sign of the Cotton effect is inverted with a specific rotation value change from -87.5 to 27.8° due to transition between two discrete conformations, a kinetically controlled structure formed upon polymerization and a thermodynamically more stable structure.[34]

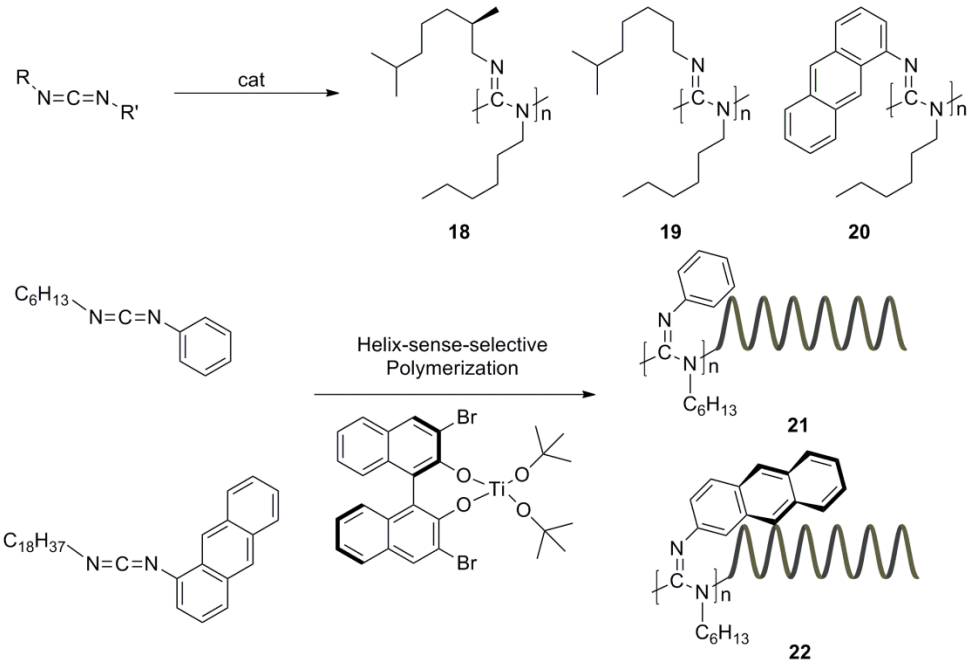


14 **15** **16** **17**

A.1.3. Polyguanidines

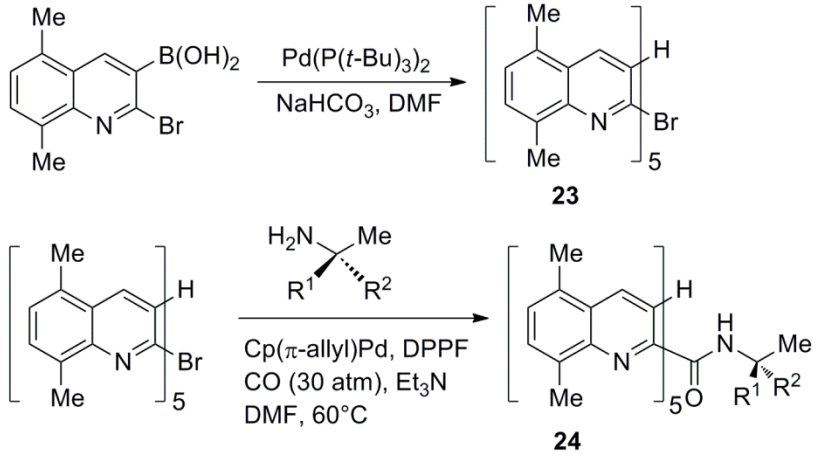
Polyguanidines were considered dynamic helical polymers due to a rapid helix inversion until Novak et al. found an increased specific rotation value in solution at elevated temperature. This behavior is due to conformational change from a kinetically formed structure to a thermodynamically stable helical.[35-36] Optically active polyguanidines were

prepared by polymerization of optically active bulky carbodiimide with achiral titanium(IV) catalysts **18**-**20** or by helix-sense-selective polymerization of achiral monomers with chiral binaphthol titanium(IV) catalysts **21** and **22**.[37-39] The anthracene- containing polyguanidines racemize slowly in toluene at 80 °C, suggesting a high inversion barrier.



A.1.4. Poly(quinoxaline-2,3-diyl)s

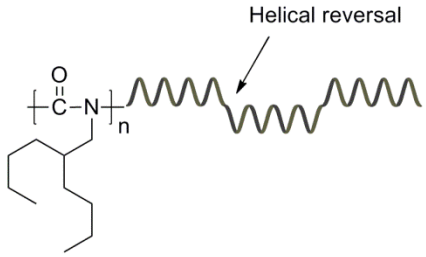
Suginome et al. have synthesized oligo(quinolone-2,3-diyl)s **23** and **24** by Suzuki-Miyaura coupling reaction. A 5/2 helix with an average dihedral angle of 127° between adjacent quinolone rings was found by single-crystal X-ray analysis. Introduction of optically active amide groups successfully induced a one-handed helix.[40]



A.2. Dynamic Helical Polymers

A.2.1. Polyisocyanates

Polyisocyanates adopt an 8/3 helical conformation due to the conjugated, partial double-bond nature of the peptide backbones. Due to the low inversion barrier, they consist of interconvertable right- and left-handed helical segments separated by rare helical reversals.[12, 41]



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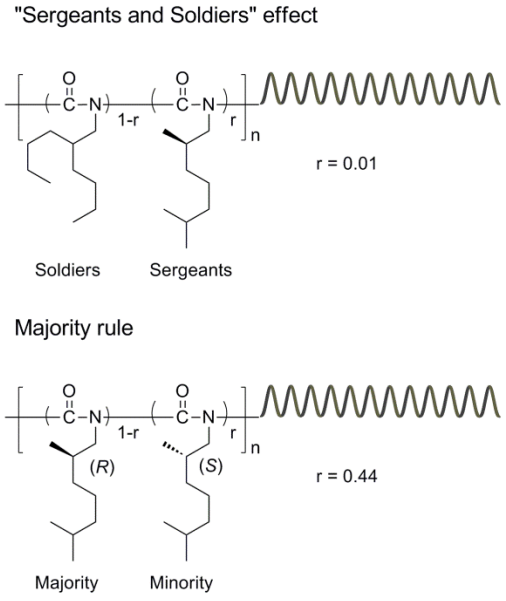
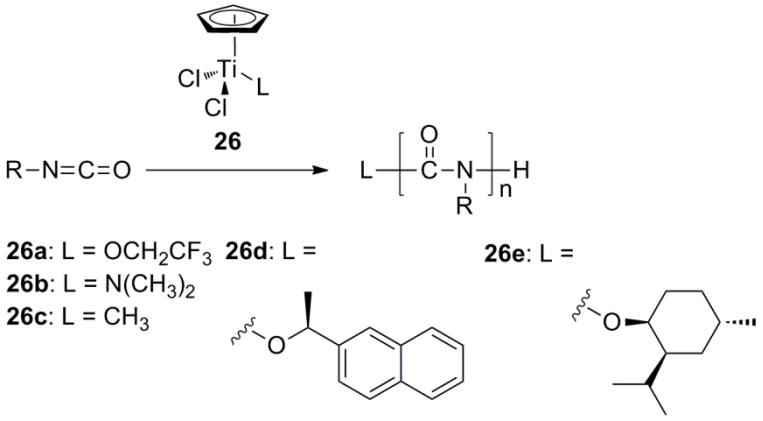
Optically active polyisocyanates can be obtained by copolymerization of an achiral isocyanate with a small amount of a chiral isocyanate or by polymerization of achiral cyanates with optically active initiators ("Sergeants and Soldiers" effect).[42-44] Green et al. found that isocyanates consisting of (*R*)- and (*S*)-enantiomers with small enantiomeric excess (ee) induce a single-handed helical polymer for poly(2,6-dimethylheptyl isocyanates ("majority rule").[45]

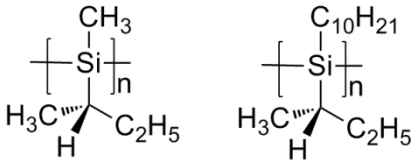


Novak et al. reported poly(alkylisocyanate)s with controlled molecular weight and narrow molecular weight distribution using organotitanium(IV) complexes for living polymerization of alkyl isocynates.[46-48] It is known that the alkoxy group of the Ti(IV) catalyst **26** initiates the polymerization.



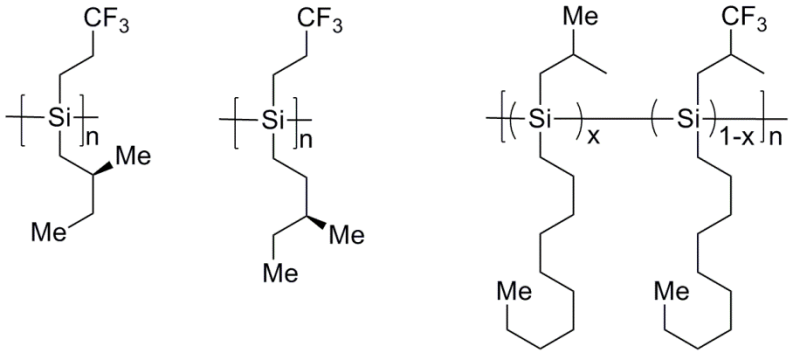
A.2.2. Polysilanes

Polysilanes adopt a 7/3 helical conformation.[49-50] This class of polymers has a unique chromophoric and fluorophoric σ-conjugated silicon-silicon backbone due to σ_{Si}-σ_{Si}* transition around 300-400 nm. Polymers **27** and **28** were synthesized by the Na-mediated condensation reaction of chiral dichlorosilanes in the presence of 15-crown-5. Whereas coexisting right- and left-handed helices were found in polymer **27**, one-handed helical conformation is induced in polymer **28**. Polymer **27** exhibits a positive and negative peak in its CD spectra and the fluorescent anisotropy depends strongly on the wavelength suggesting the existence of right- and left-handed helices. Polymer **28** shows a narrow absorption peak, a CD peak with a spectral profile supporting the presence of a single-helical conformation.[49-51]



27 **28**

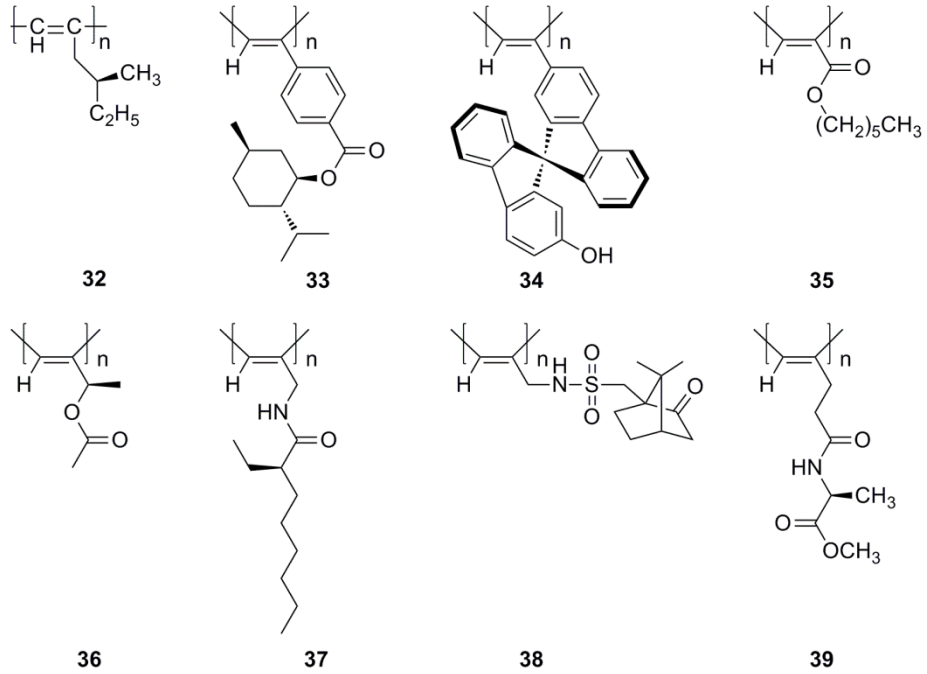
Fujiki et al. reported that the weak intramolecular cooperative interaction between C-F···Si can induce helical conformation. 3,3,3-trifluoropropyl is ineffective to induce helical conformation of polysilanes with the chiral *β*-branched alkyl substituents in polymer **29**. In contrast, CD spectra of polymer **30** showed the typical characteristics of a stable helical chain suggesting the presence of weak intramolecular C-F···Si interactions. Copolymer **31** having 3,3,3-trifluoropropyl and n-decyl side chains forms an organogel in nonpolar organic solvents. IR measurements and the analysis of a model silane molecule support the theory that C-F···Si interaction is responsible for helical conformation.[52-54]



29 **30** **31**

A.2.3. Polyacetylenes

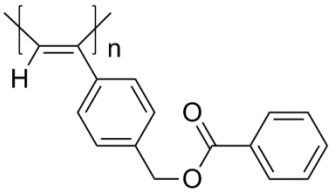
After the discovery of the first optically active polyacetylene **32** from (*S*)-4-methyl-1-hexyne by Ciardelli and co-workers, a large number of optically active dynamic helical polyacetylenes has been synthesized. The examples include phenylacetylenes (**33**, **34**), propionic esters (**35**), propargyl esters (**36**), *N*-propargylamides (**37**), *N*-propargylsulfamide (**38)** and acetylenes having amino acid moieties (**39**).[55-62]



32 **33** **34** **35**

36 **37** **38** **39**

A series of *cis*-poly(phenylacetylene)s has been prepared from self-assembling dendrons bearing chiral or achiral peripheral alkyl chains. Most *cis*-poly(phenylacetylene)s are thermally unstable in solution due to cis-trans isomerization, and irreversible intramolecular 6π-electrocyclization of the 1,3-*cis*-5-hexatriene followed by chain cleavage and subsequent release of the 1,3,5-triphenylbenzene derivatives. However, the dendronized *cis*-poly(phenylacetylene)s **40**-**42** showed a thermal stability even at 100°C.[63-65]



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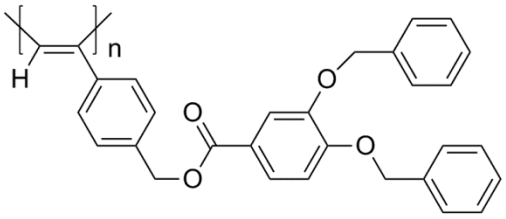

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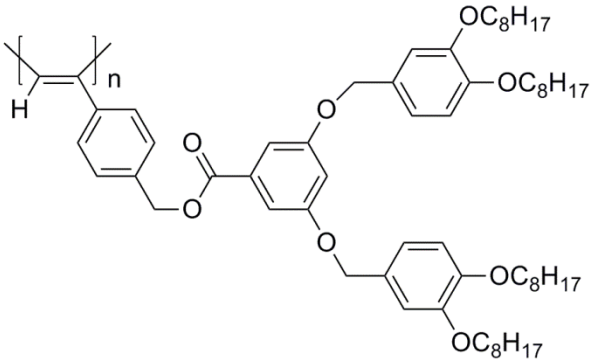

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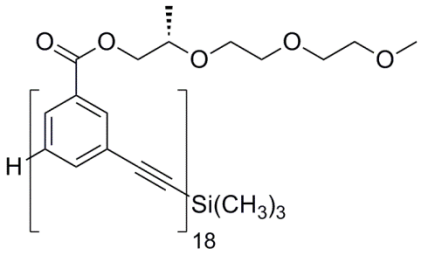
A.3. Foldamer-Based Helical Polymers

A.3.1. Poly(*m*-phenylene ethynylene)s

Moore et al. have developed optically active oligo(m-phenylene ethynylene)s **43** with chain lengths of more than eight repeat units which fold into a helical conformation. This process which is thermodynamically driven by solvophobic effects.[14] These oligomers can fold into a preferred-handed helical conformation in the presence of the specific guest (-)-α-pinene. The polymer **44** bearing the chiral side group based on L-alanine induced a left-handed helical conformation. This polymer can be used as template for supramolecular helical aggregates of cyanine dyes, which are believed to groove-bind to the periphery of the polymer helix.[66] A Poly(m-phenylene ethynylene)-based polyradical bearing chiral pinanyl groups has been synthesized (**45**).[67] Cotton effects are observed in the absorption region of the backbone of the hydrogalvinoxyl chromophore when it is dissolved in ethyl acetate, indicating an excess of a one-handed helical foldamer conformation. Poly(m-phenylene ethynylene)s having a (+)-menthyl group **46** is optically active with the magnitude of CD bands varing in the presence of (+)- or (-)-menthol in chloroform, suggesting that it has a chiral recognition ability.[68] Poly(*m*-phenylenedisilanylene) **47** adopts the biased twist sense of the helical conformations through the complexation with appropriate metal ions.[69]



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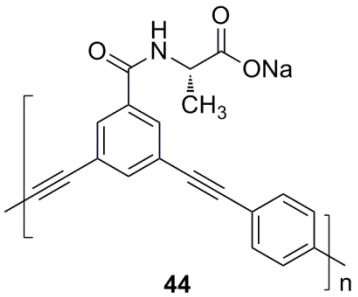

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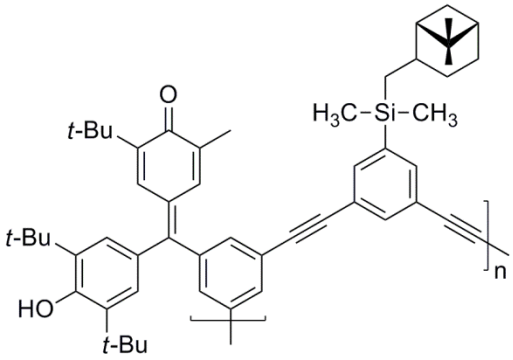

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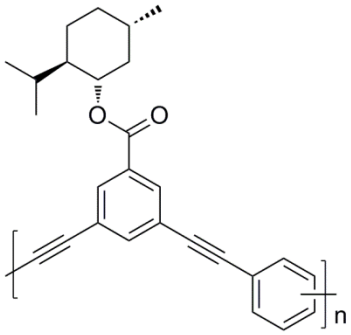

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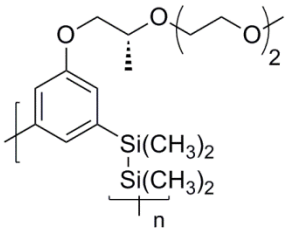
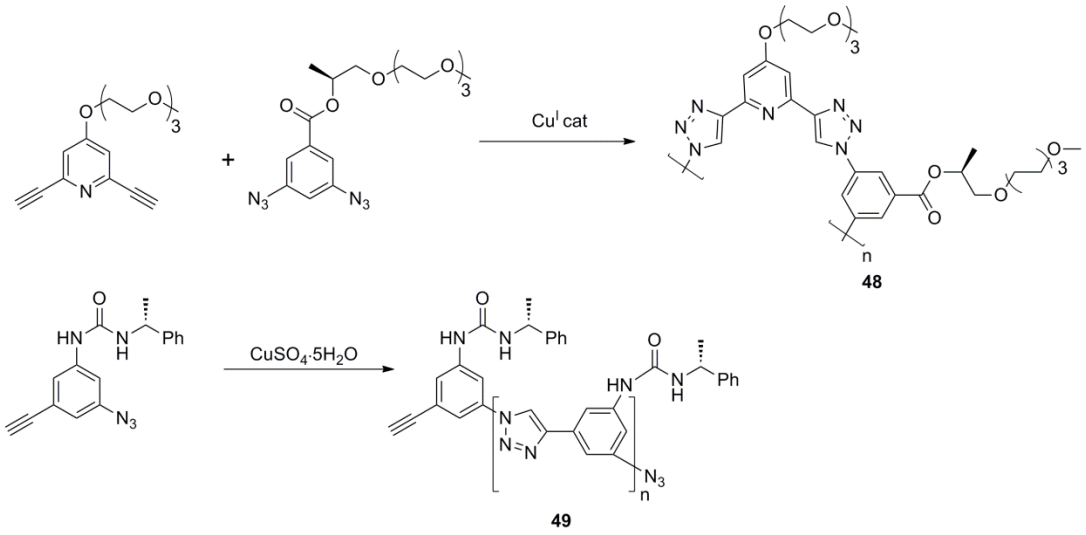


47

A.3.2. Click Polymerization

The Cu-catalyzed 1,3-dipolar cycloaddition of azides and alkynes, frequently referred to as Click reaction, was used to synthesize various optically active polymers.[70-72] Strong preference for the kinked *anti-anti* conformation of the 2,6-bis(1,2,3-triazol-4-yl)pyridine units in the main chain induces a helical conformation. This polymer **48** adopts a helical conformation in both polar and non-polar solvents with a large degree of pre-organization in the polymer due to the presence of 2,6-bis(1,2,3-triazoyl-4-yl)pyridine units.[70]

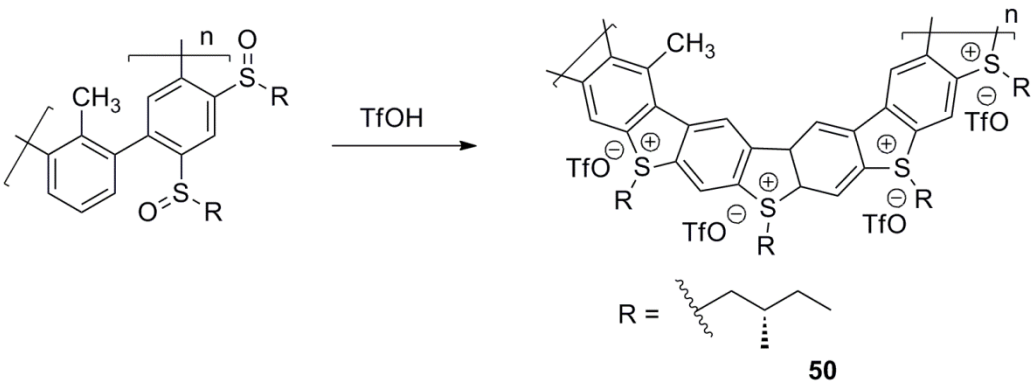


Similarly, an optically active monomer bearing an azide group within the molecule was synthesized. The Cu catalyst promotes click polymerization and gives an optically acitive polymer bridged by the *anti*-1,2-3-triazole-ring. This polymer **49** displays CD signals in the π-conjugated main chain region in poor solvents, accompanied by a fluorescent color change due to the formation of π-stacked supramolecular chiral aggregates.[72]

A.3.2. Ring-Closing Reaction

A regioselective intramolecular ring-closing reaction has been used to construct a helicene-like ladder polymer **50** with a controlled helical sense from a flexible linear polymer.[73] The ladder polymer does not show any Cotton effect in the CD spectra when dissolved in dichloromethane, DMF or DMSO, but Cotton effects are observed in a mixture of chloroform and acetonitrile (a poor solvent). Electron transmittance along the helical π-conjugation under a lower bias voltage occurs when the electronic conduction of **50** based on a nanometer-sized electronic device is stimulated.

Chiral sulfoxide without chiral alkyl substituents has been polymerized and the resulting polymer **51** displays a characteristic CD signal due to π-π* transition.[74]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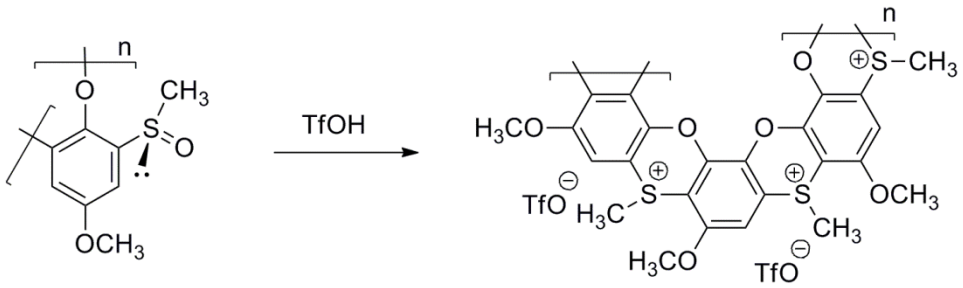
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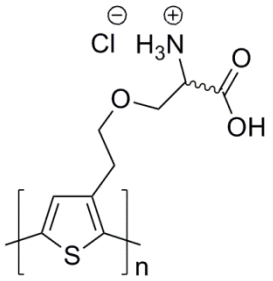
CH3
H3CO
TfO

51

A.4. Other Types of Helical Polymers

A.4.1. π-Conjugated Helical Polymers

Polythiophenes usually exhibit optical activity in the π-π* transition region. They are optically active when the polymer chains are forming supramolecular, π-stacked self-assembled aggregates in a poor solvent or at low temperature, whereas they usually show no CD signal in the UV-vis region in a good solvent or at high temperature.[75-76] A conjugated polythiophene with a free amino acid side chain has been prepared from the monomer **52**. The chirality of the zwitterionic side chain induced a right- and left-handed helical form of polythiophene.[77-79]



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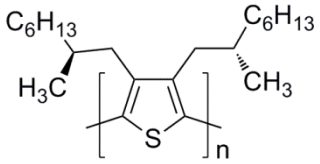


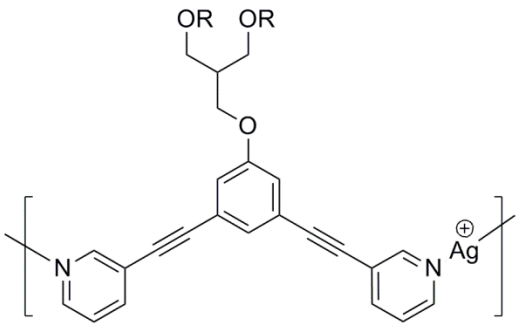
53

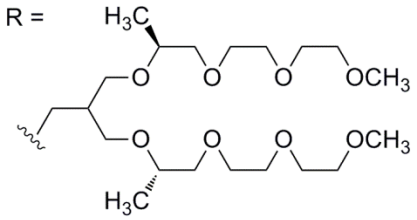
Dialkyl-substituted chiral polythiophene **53** has been synthesized.[80]

A.4.2. Metallosupramolecular Helical Polymers

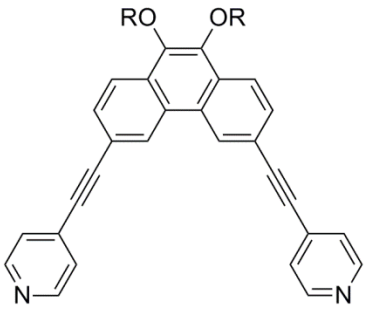
A bent-shaped bipyridine ligand containing a dendritic aliphatic side chain **54** has been synthesized and complexed with silver ions through a self-assembly process by Lee and co-workers.[81-84] The resulting complexes self-assemble into folded helical chains when small counter anions such as nitrate and tetrafluoroborate are introduced. The complexes with larger anions transform the folded helical chain into dimeric cycles or unfolded linear chain conformations. These results suggest that the secondary structure can be regulated by a systematic variation in the size of the counteranion.

A helical spring which has a switchable pitch has been prepared from the aqueous self-assembly of dipyridyl ligands with silver ions.[82] This polymer **55** adopts a helical conformation that displays reversible extension-contraction motions, triggered by temperature. This dynamic conformational change leads to a switch between the fluorescent stretched and the nonfluorescent compressed state of the supramolecular springs by breaking the intramolecular π-π stacking interactions in the polymer backbone.[83]

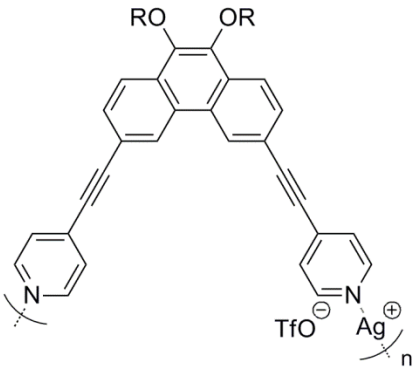

OR
OR
O
N
Ag
N


R =
H3C
O
O
O
OCH3
O
O
O
OCH3
H3C

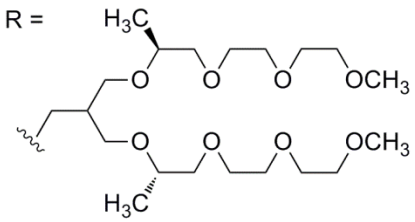
54

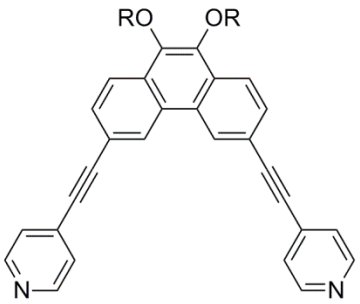

RO
OR
N
N


AgOTf

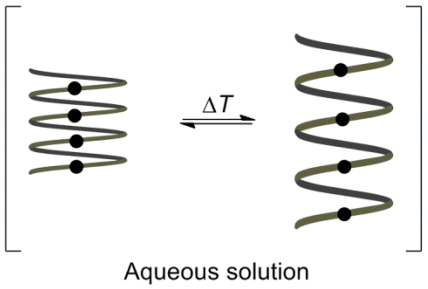

RO
OR
N
N
TfO
Ag
n

55


R =
H3C
O
O
O
OCH3
O
O
O
OCH3
H3C


RO
OR
N
N


AgOTf


ΔT
Aqueous solution

55

A.5. Scope of Thesis

The first objective of this thesis is the synthesis of optically active polyolefins. The second is to develop styrene/butadiene block and styrene/ethylene block copolymers using the living character of polymerization with a zirconium catalyst having a cyclohexyl-bridged (OSSO)-type ligand.

Chapter 2 describes the development of optically active crosslinked homochiral polystyrene and oligostyrenes. Homochiral polystyrenes are crosslinked to induce a helical structure in solution and the chiral recognition ability is investigated. Optically active oligostyrenes are crosslinked and relations between optical activity and the degree of crosslinking are described.

In chapter 3, the synthesis of optically active polynorbornenes is described. Polymerization results for norbornene and the optical activities of polynorbornenes are reported. Results of hydrooligomerization and deuteriooligomerization to investigate tacticity and structure of polynorbornene are described.

Chapter 4 describes the block copolymerization of styrene and butadiene using zirconium and titanium catalysts with an (OSSO)-type ligand. The preparation of a styrene/ethylene block copolymer via hydrogenation of styrene/butadiene block copolymer is described. The preparation of a butadiene oligomer using 1-hexene as a chain transfer agent is reported.

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B. Results and Discussion

B.1. Crosslinking of Homochiral Isotactic Polystyrene and Oligostyrene

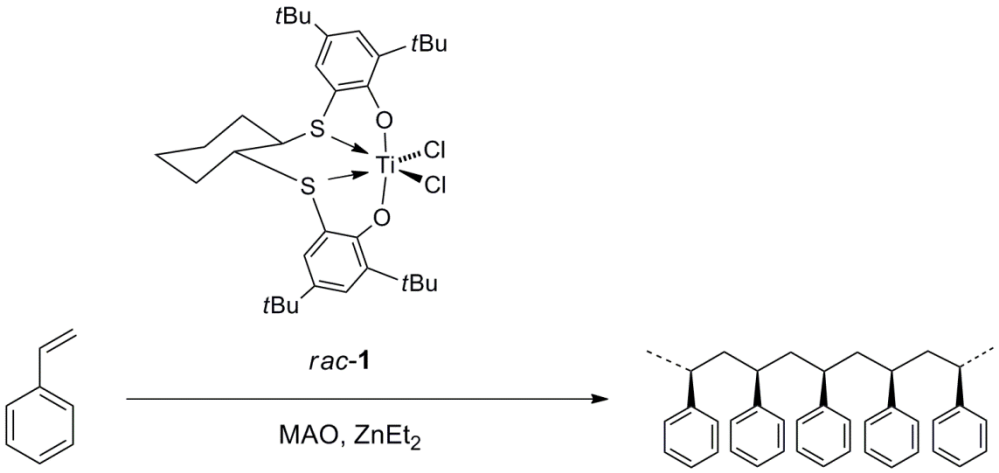
B.1.1. Introduction

Lightly cross-linked gel type polystyrene is mainly used due to its common availability and low cost. Crosslinked polystyrene gels are produced by copolymerization-crosslinking of styrene and divinylbenzene or by introducing additional crosslinking bridges on the styrene copolymer by Friedel-Crafts reactions.[1-5] Polystyrene gel produced by Friedel-Crafts reaction has a homogeneous porous structure and high surface area to weight ratio.[6-11] The swelling property of gel type polystyrene causes a phase change from a solid to a solvent-swollen gel, which allows diffusion of reactants to reaction sites through a solvent-swollen gel network. Polystyrene gels are used as stationary phase in column chromatography or as polymeric support for olefin polymerization as well as in solid-phase peptide synthesis.[12-17] Previously, Okuda *et al.* have reported that configurationally rigid bis(phenolato) titanium catalysts derived from the (OSSO)-type ligand efficiently polymerize styrene to give chiral isotactic polystyrenes.[18-22] These are prepared using a chiral titanium catalyst based on the (OSSO)-type phenol and 1-hexene as a chain transfer agent. The specific rotation value depends on the number average molecular weight of the isotactic polystyrenes.[23-24] In this study, chiral isotactic crosslinked polystyrenes and oligostyrene gels are synthesized to prepare polymers with optical activities.

B.1.2. Results and Discussion

B.1.2.1. Preparation of Isotactic polystyrene

Isotactic polystyrene is prepared using a catalyst derived from Ti(IV) dichloro complexes with (OSSO)-type ligands. The molecular weight is regulated by using diethyl zinc as a chain transfer agent. With increasing amount of diethylzinc, the molecular weight decreased. The ^{13}C NMR spectra of the polystyrenes show high isotacticity.



Scheme 1. Preparation of isotactic polystyrene.

Table 1. Polymerization of styrene using catalyst *rac*-**1**.

Run	Styrene (mmol)	Catalyst (μmol)	$ZnEt_2$ (mmol)	M_n	M_w/M_n	Conversion (%)
1	174	5.0	0	866,430	1.30	38
2	87	2.5	0.8	111,760	1.76	32
3	87	2.5	1.0	53,296	1.72	40

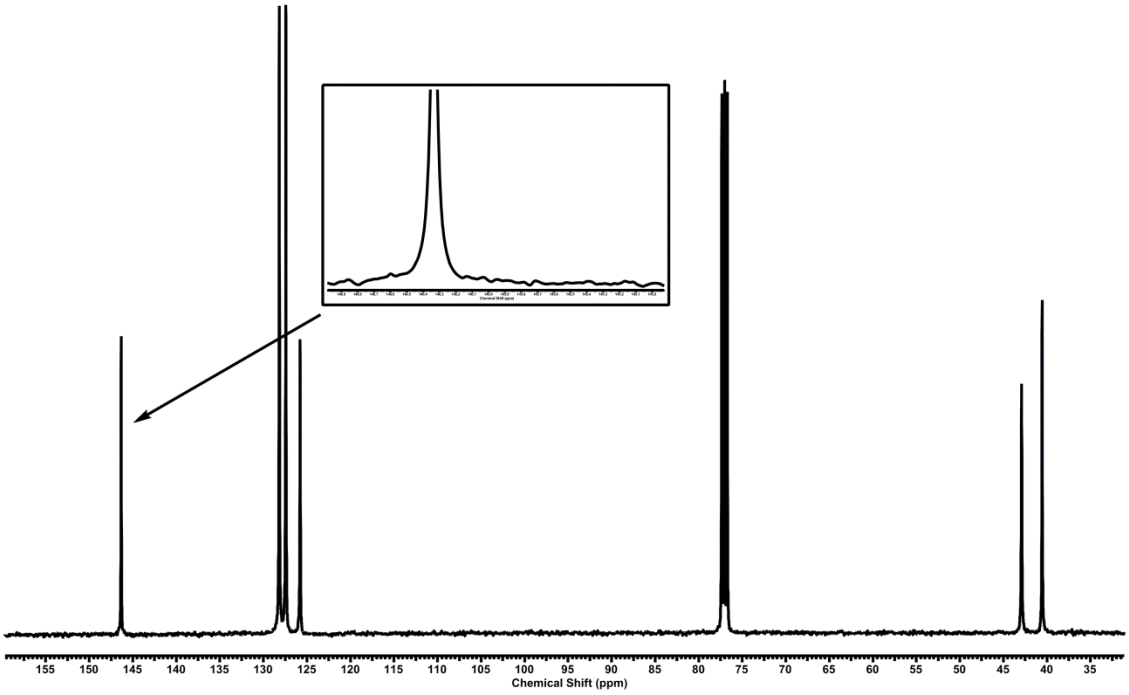


Figure 1. ^{13}C NMR spectrum of isotactic polystyrene in $CDCl_3$ at 25 °C.

B.1.2.2. Crosslinking of Polystyrene

Isotactic polystyrene was crosslinked via Friedel-Crafts reaction using 1,4-bis(chloromethyl)-2,5-dimethylbenzene as a crosslinker in nitrobenzene. Minimum amount of nitrobenzene is used to reduce the probability of forming an intrachain reaction between 1,4-bis(chloromethyl)-2,5-dimethylbenzene and phenyl groups of the same chain. When more than 5 % of the crosslinker is used, the product becomes insoluble in any organic solvent, and its characterization by NMR spectroscopy becomes impossible. As the amount of crosslinker decreases, yield increases.

Table 2. Crosslinking of isotactic polystyrene

Run	Crosslinker (mol %)	Yield (%)	Solubility in chloroform
1	10	28	insoluble
2	5	60	insoluble
3	2	75	swollen
4	0.5	100	swollen
5	0.1	86	swollen

When less than 2 mol % of 1,4-bis(chloromethyl)-2,5-dimethylbenzene are used, crosslinked product forms as a gel in chloroform, toluene or THF and is insoluble in hexanes. Crosslinked isotactic polystyrene was extracted with soxhlet apparatus with chloroform overnight and only a trace amount of product is soluble in chloroform. ^{1}H NMR spectra of solvent swollen polystyrene show broadening of peaks as the amount of crosslinker increases due to restricted of mobility of individual chains.[25-26]

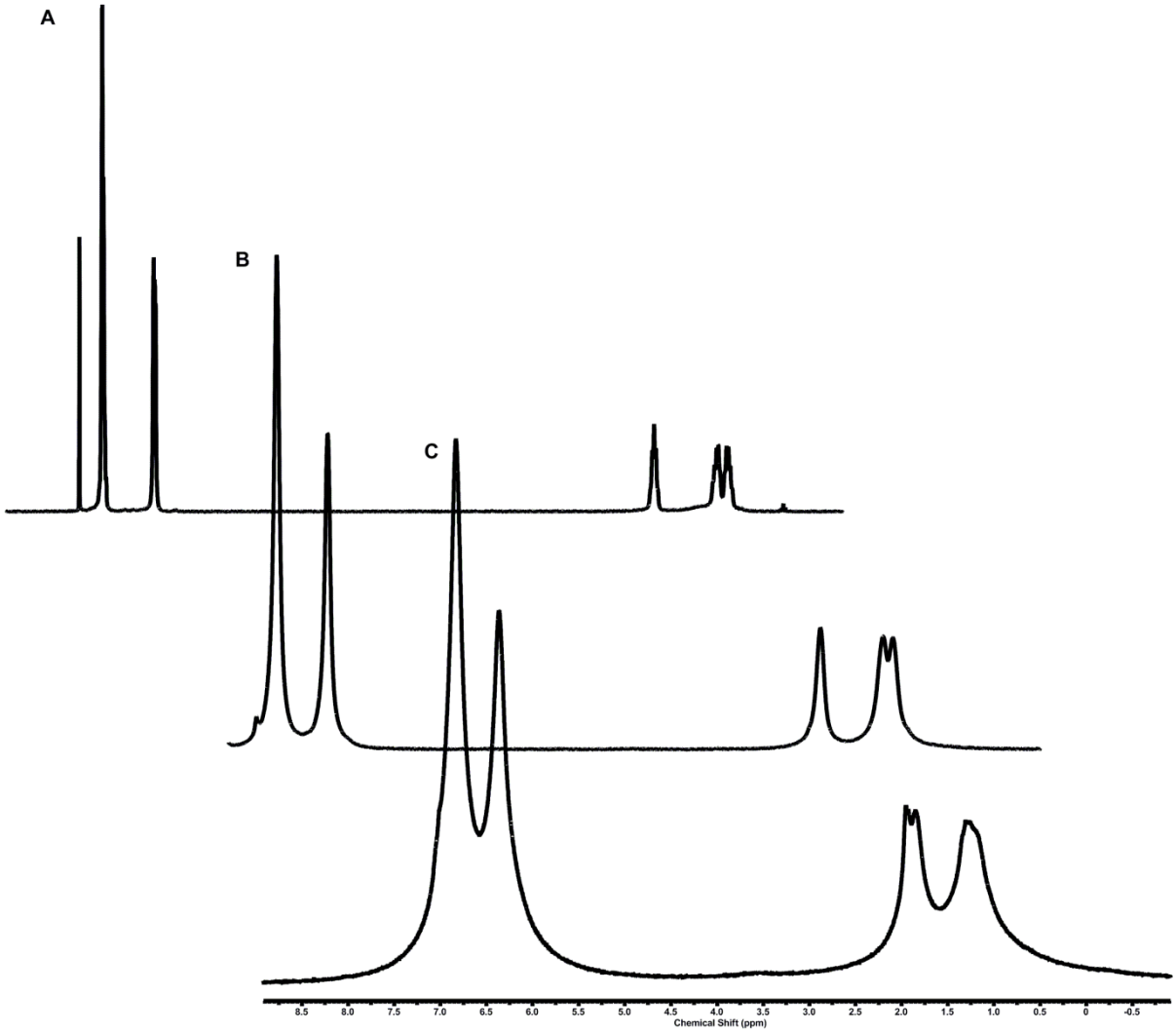


Figure 2. ^{1}H NMR spectra ($CDCl_3$, 25 °C) of isotactic polystyrene (A), crosslinked isotactic polystyrene gel incorporating 0.5 mol % of 1,4-bis(chloromethyl)-2,5-dimethylbenzene (B), crosslinked isotactic polystyrene gel incorporating 2 % of 1,4-bis(chloromethyl)-2,5-dimethylbenzene (C)

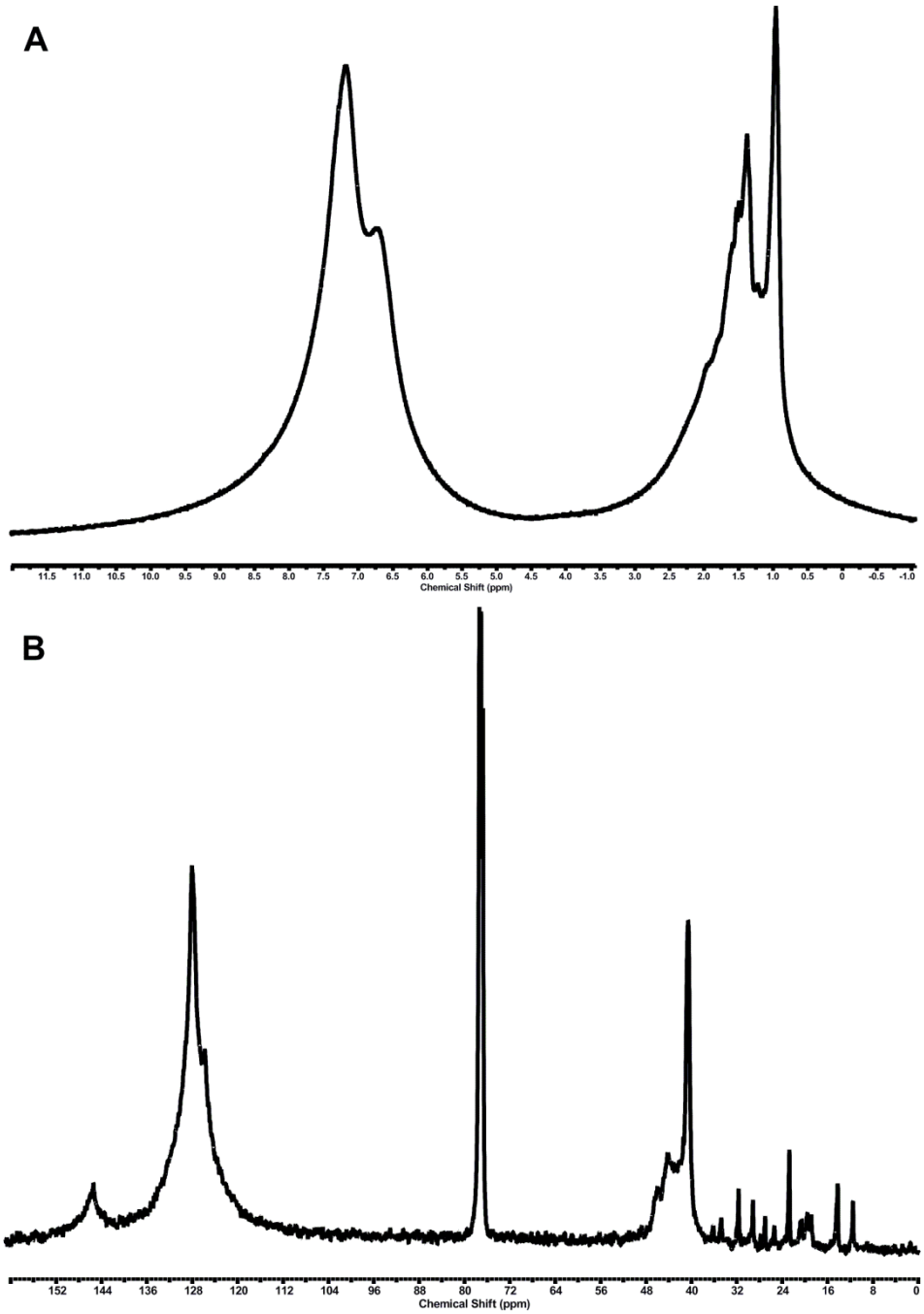


Figure 3. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of 5 mol % crosslinked atactic polystyrene (A), ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of 5 mol % crosslinked atactic polystyrene (B).

Due to the insolubility of crosslinked isotactic polystyrene, a ^{13}C NMR spectrum could not readily be recorded. To detect peaks due to the crosslinker, the more soluble atactic polystyrene was crosslinked. But still the peaks of crosslinker were not found in the ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR spectrum of solvent swollen polystyrene shows broadening of peaks as the ^{1}H NMR spectrum of crosslinked isotactic polystyrene (Figure 3).

The crosslinking reaction can be also conducted in suspension to avoid a crushing process.[27-29] It is observed that most swollen particles are in a spherical form due to the action of silicone oil as the suspending medium (Figure 4).

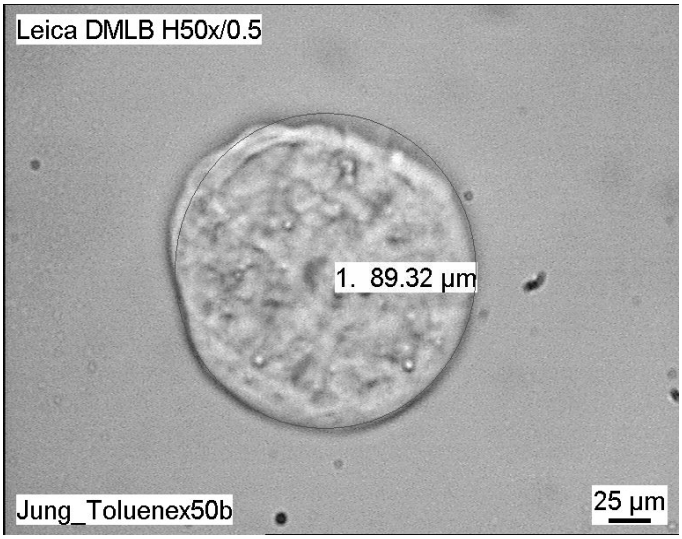


Figure 4. Micrography of the appearance of crosslinked polystyrene suspension in toluene.

To prove the possibility of employing polystyrene as a column packing material, crosslinked isotactic polystyrene was swollen in toluene using a packed column (20 x 1.5 cm) and methylorange was loaded. Solvent penetrated the swollen gel due to the pores formed by crosslinking. The methylorange layer moved with increased polarity of the elution solvent. Thus isotactic polystyrene interacts with methylorange. This result suggests that the crosslinked isotactic polystyrene can be used as a material for column chromatography. It is tested whether chiral isotactic polystyrene has chiral recognition ability. It is known that even though polystyrene has a helical conformation in solid state, it loses most of its conformational rigidity in solution.[30-32] However, polystyrene might maintain its conformational stability after crosslinking because the mobility of chain decreases on the crosslink junction. Racemic *trans*-stilbene oxide, Tröger's base or flavanone were loaded on the swollen chiral isotactic polystyrene, eluted with toluene and each fraction was analyzed with chiral HPLC. Each fraction shows statistical distributions of enantiomeric excess within 2% error. Thus chiral isotactic polystyrene shows no chiral recognition ability.

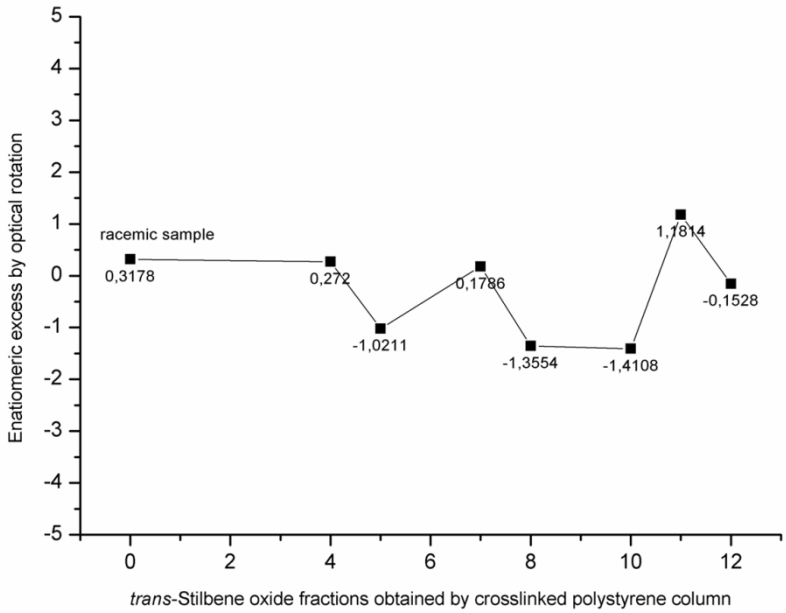
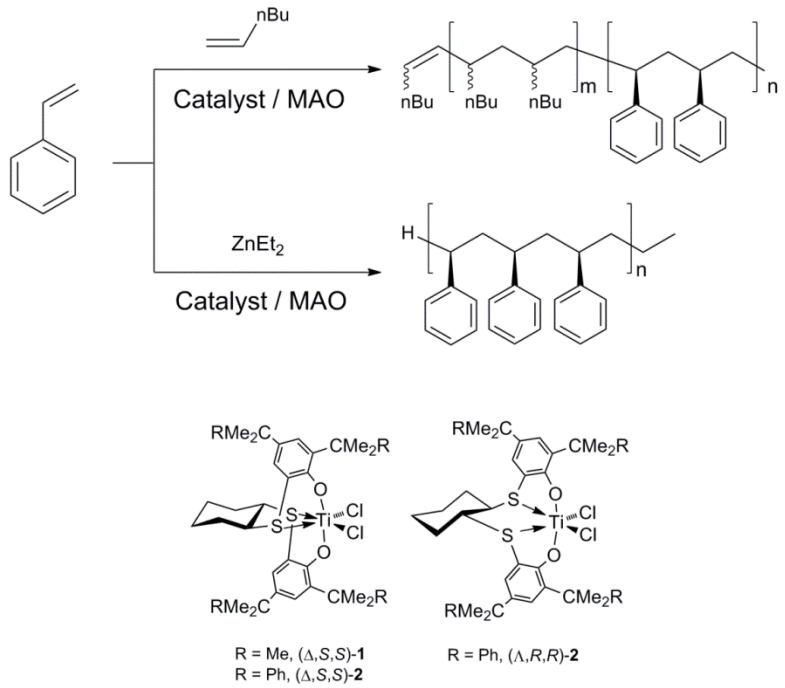


Figure 5. Analysis of *trans*-stilbene oxide fractions obtained by crosslinked polystyrene column using HPLC.

B.1.2.3. Synthesis of Crosslinked Isotactic Oligostyrenes

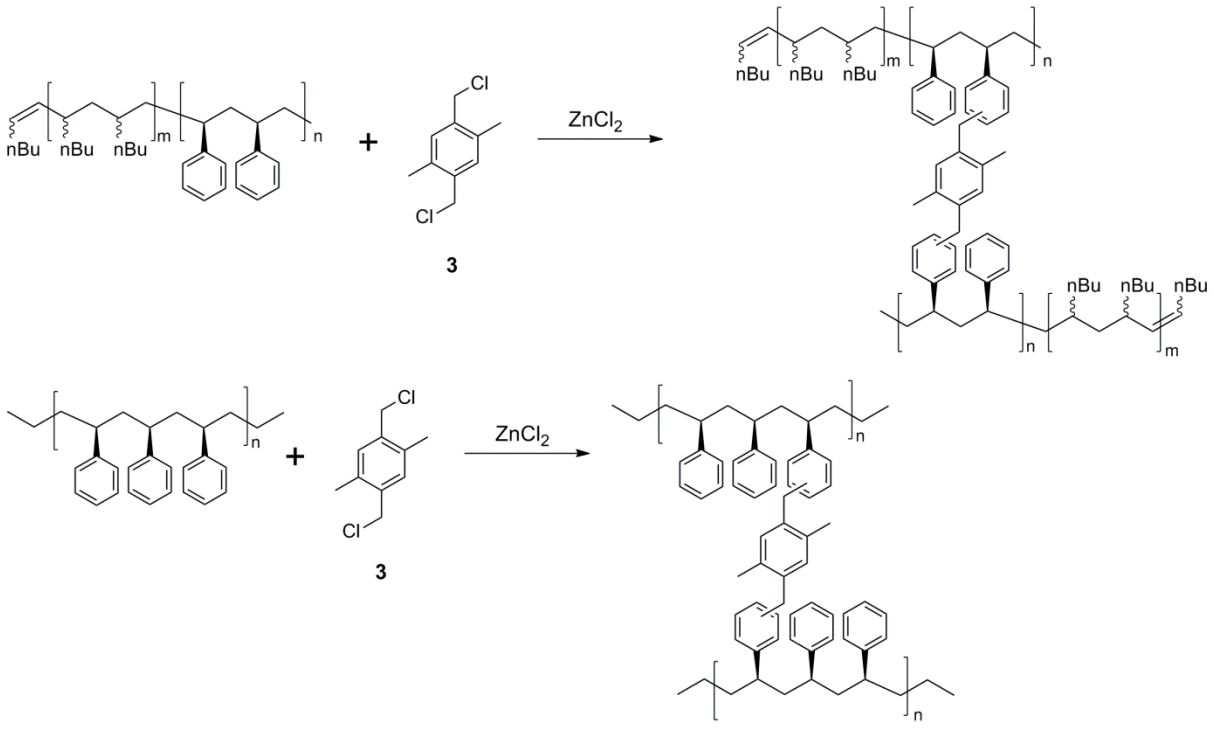
Chiral isotactic oligostyrenes are prepared according to literature procedure (Table 3).[23-24]



Scheme 2. Synthesis of chiral isotactic oligostyrene.

Table 3. Preparation of chiral oligostyrenes.

Catalyst	[Styrene] (mol/L)	[1-Hexene] (mol/L)	Et_2Zn : Ti	Yield (mg)	M_n	M_w/M_n	$[\alpha]_D^{23}$
(*Δ*,*S*,*S*)-**1**	1.6	1.4	-	373	5,133	1.51	+1.5
(*Δ*,*S*,*S*)-**2**	1.6	1.4	-	1,004	2,628	1.52	+0.8
(*Δ*,*S*,*S*)-**2**	1.6	2.3	-	690	2,113	1.33	+1.4
(*Λ*,*R*,*R*)-**2**	1.6	2.3	-	888	1,819	1.32	+2.4
(*Δ*,*S*,*S*)-**1**	0.97	-	7,392	213	3,745	1.73	-2.6
(*Δ*,*S*,*S*)-**2**	0.97	-	7,392	1,090	14,942	1.77	-0.6
(*Λ*,*R*,*R*)-**2**	0.97	-	7,392	1,260	13,787	1.75	+1.5



Scheme 3. Crosslinking of isotactic polystyrene and oligostyrene.

Chiral oligostyrene is crosslinked in the same way as polystyrene. The amount of crosslinker needed for gelation is investigated using racemic oligostyrenes to measure optical activities. Due to the low molecular weight of oligostyrenes, a higher amount of crosslinker is needed for gelation. Oligostyrene having a number average molecular weight 2,457 needed 8.3

mol % of crosslinker for gelation. With increasing number of crosslinkers, the molecular weight distribution becomes broader.

Table 4. Gelation point of chiral oligostyrenes.

[Styrene] (mol/L)	[1-Hexene] (mol/L)	Yield (mg)	M_n	M_w/M_n	Crosslinker mol % until gelation
1.6	1.4	380	5,311	1.54	5.1
1.6	4.5	303	2,457	1.34	8.3

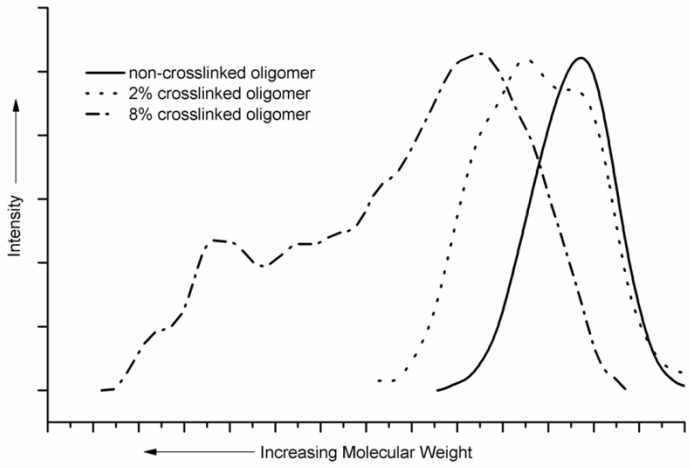


Figure 6. GPC elugram of an *i*PS oligomer and the corresponding crosslinked oligomers. Solid line: Non-crosslinked oligostyrene (M_n = 1,997 g/mol; M_w/M_n = 1.3); dotted line: 2 % crosslinked oligostyrene (M_n = 2,929 g/mol; M_w/M_n = 1.74); dash dotted line: 8 % crosslinked oligostyrene (M_n = 12,234 g/mol; M_w/M_n = 9.09).

Due to the soluble nature of oligostyrenes below the gelation point and the higher amount of crosslinker in the product, signals of crosslinker were found in NMR spectra. ^{1}H NMR spectrum of crosslinked oligostyrenes show a broad singlet in the region of 3.5–4.0 ppm which is assigned to the methine protons of the crosslinking bridge, consistent with the shift of methine protons of diphenylmethane (3.93 ppm). The integral increased with the amount of crosslinker. In addition, ^{13}C NMR spectra show peaks in the region of 130–135 ppm and these peaks were assigned to the phenyl carbons of the crosslinking bridge.

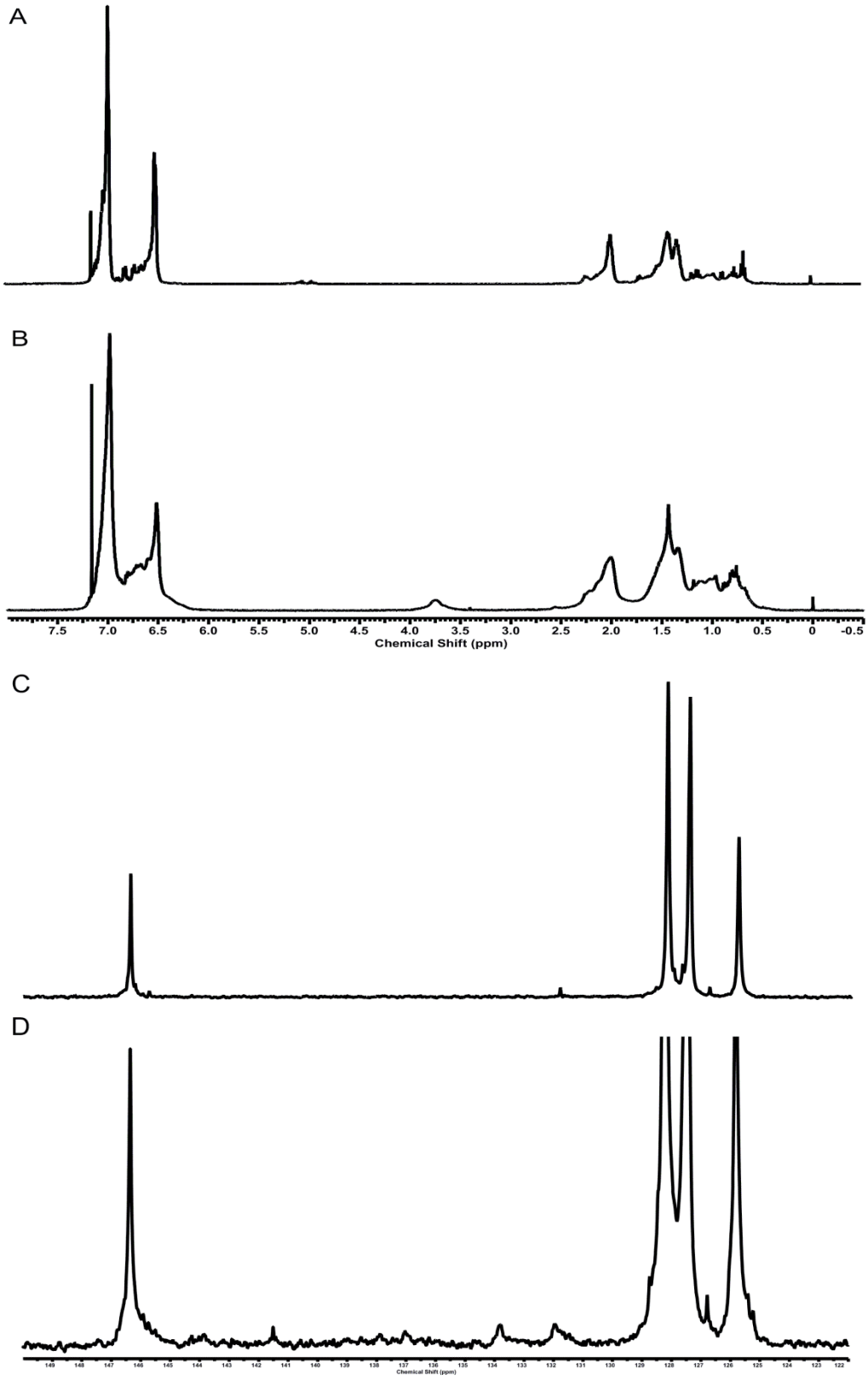


Figure 7. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of isotactic oligostyrenes with oligo(1-hexene) terminal groups (A), crosslinked isotactic oligostyrene incorporationg 7% of 1,4-bis(chloromethyl)-2,5-dimethylbenzene (B), ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of isotactic oligostyrenes with oligo(1-hexene) terminal groups (C), and crosslinked isotactic oligostyrene incorporationg 7% of 1,4-bis(chloromethyl)-2,5-dimethylbenzene (D).

B.1.2.4. Optical Activities of Oligostyrenes

Specific rotations of oligostyrenes could be measured because chiral isotactic oligostyrenes crosslinked below the gelation point are soluble in chloroform. Even if oligostyrenes are crosslinked, they are optically active (Table 5).

Table 5. Specific rotations of chiral oligostyrenes and crosslinked oligostyrenes

Catalyst	Chain transfer agent	M_n	M_w/M_n	**3** (mol %)	$[\alpha]^{23}_D$
(Δ,*S*,*S*)-**1**	1-Hexene	5,133	1.51	0	+1.5
		9,135	2.05	2	+0.4
		12,234	9.10	4	-0.4
(Δ,*S*,*S*)-**2**	1-Hexene	2,113	1.33	0	+1.4
		2,929	1.74	2	-1.3
		5,966	3.31	6	-0.4
		10,172	1.51	8	+0.8
(Δ,*S*,*S*)-**2**	1-Hexene	2,628	1.52	0	+0.8
		4,495	1.85	2	-0.6
		16,577	4.45	6	+0.7
(Λ,*R*,*R*)-**2**	1-Hexene	1,819	1.32	0	-1.1
		2,831	1.68	2	+1.2
		4,384	2.15	4	+1.9
		11,331	4.39	7	+0.6
(Δ,*S*,*S*)-**1**	Et_2Zn	3,745	1.73	0	-2.6
		13,196	6.31	4	-0.9
(Δ,*S*,*S*)-**2**	Et_2Zn	14,942	1.77	0	-0.6
		25,161	2.17	0.5	-0.6
		28,252	9.27	1	-0.1
(Λ,*R*,*R*)-**2**	Et_2Zn	13,787	1.75	0	+1.5
		14,864	2.21	0.5	+0.9
		20,060	2.35	1	+1.2

In the case of 1-hexene terminated crosslinked oligostyrenes from (Δ,*S*,*S*)-**1** and (Δ,*S*,*S*)-**2**, their specific rotations are decreased down to 4 % but increased with further crosslinking. Specific rotations of oligostyrenes from (Λ,*R*,*R*)-**2** show reversed trend. ^{1}H NMR spectra of crosslinked 1-hexene terminated oligostyrenes show a broad singlet in the region of 2.5–2.6 ppm that result from the reaction of terminal vinyl group with crosslinker. The integration of the signal between 2.5-2.6 ppm is similar to that of broad singlet in the region of 3.5–4.0 ppm for 2 % crosslinked 1-hexene terminated oligostyrene. But 8 % crosslinked oligostyrenes show a larger peak in the region of 3.5–4.0 ppm than between 2.5 and 2.6 ppm. These results indicate that terminal vinyl groups react faster than phenyl groups of polystyrene and decrease in specific rotations maybe due to asymmetric induction by chiral polystyrene or change of substitution group on polystyrene. Oligostyrenes produced using diethylzinc and (Δ,*S*,*S*)-**1** and (Δ,*S*,*S*)-**2** catalyst showed a reversed sign of specific rotation and the magnitude of specific rotations decreased with crosslinking. It is supposed that internal crosslinking reduced the specific rotations because oligostyrenes produced from diethylzinc have no terminal vinyl groups.

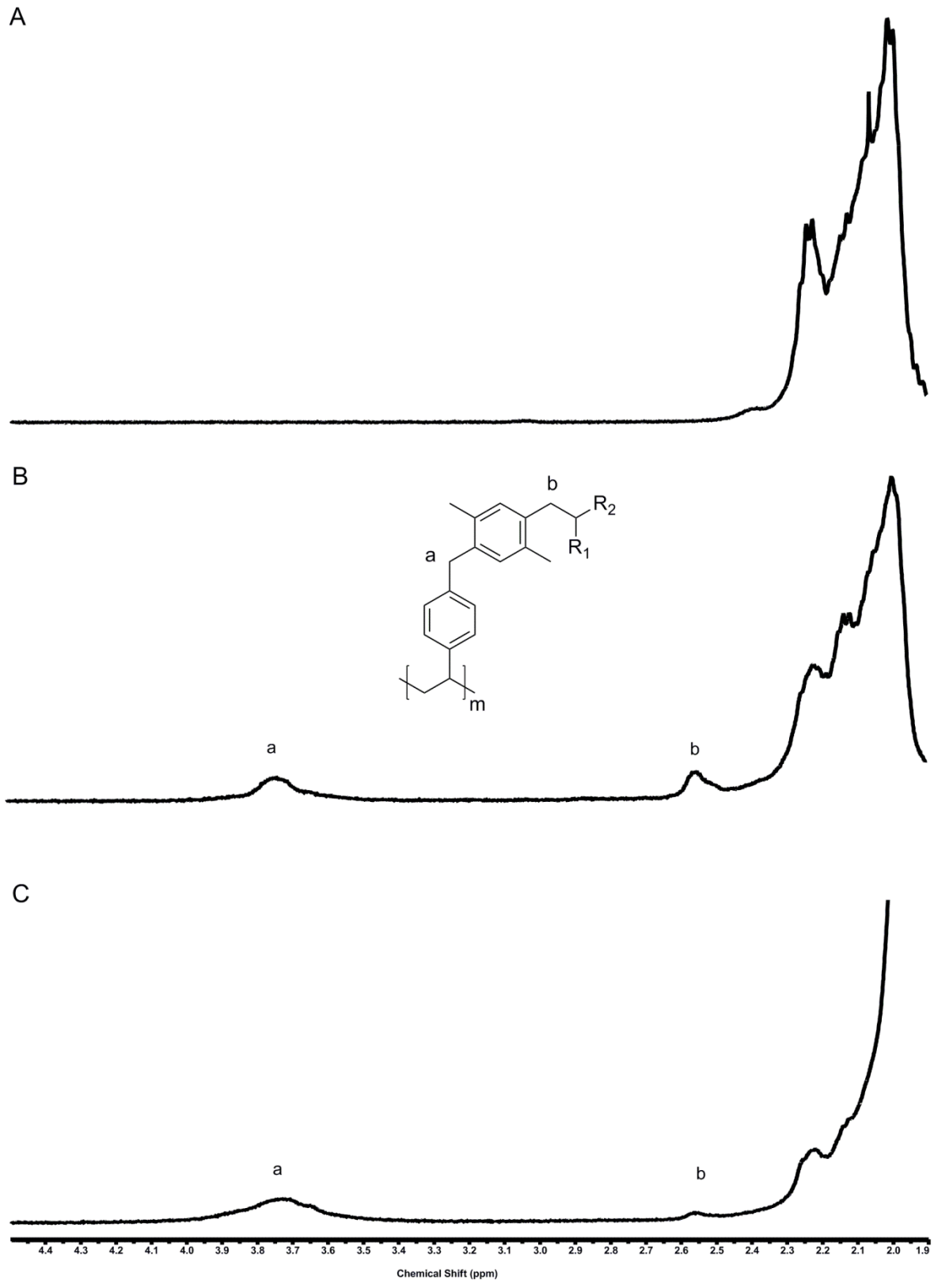


Figure 8. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of isotactic oligostyrene with oligo(1-hexene) terminal groups (A), crosslinked isotactic oligostyrene incorporating 2 % of 1,4-bis(chloromethyl)-2,5-dimethylbenzene (B), crosslinked isotactic oligostyrene incorporating 8 % of 1,4-bis(chloromethyl)-2,5-dimethylbenzene (C).

Particle sizes of chiral crosslinked oligostyrenes were determined by light scattering. Particle sizes in solution decreased as oligostyrens are crosslinked more.

Table 6. Particle size determined by light scattering.

M_n	M_w/M_n	Crosslinker (mol %)	Size[2] (nm)
1,997[1]	1.32	0	60-80
2,929	1.74	2	110
5,966	3.31	6	90
10,172	1.51	8	30-40

[1] Non-crosslinked oligostyrene was prepared. [styrene] = 1.6 mol/L, [1-hexene] = 2.3 mol/L, (Δ,*S*,*S*)-**2** = 1.25 μmol, [MAO] / [(Δ,*S*,*S*)-**2**] = 1800, toluene = 6 mL, T = 40 °C, t = 2 h. [2] Sizes are determined in toluene solution.

As the crosslinked oligostyrenes were formed to be optically active, the chiral recognition ability was investigated using a chiral absorption test.[33-35] Tröger's base or flavanone in hexane/ethanol solution were loaded on the crosslinked isotactic oligostyrene and the supernatant solution was analyzed by chiral HPLC. But the difference of enantiomeric exess between racemic polystyrene and the chiral crosslinked oligostyrene is within 2 %.

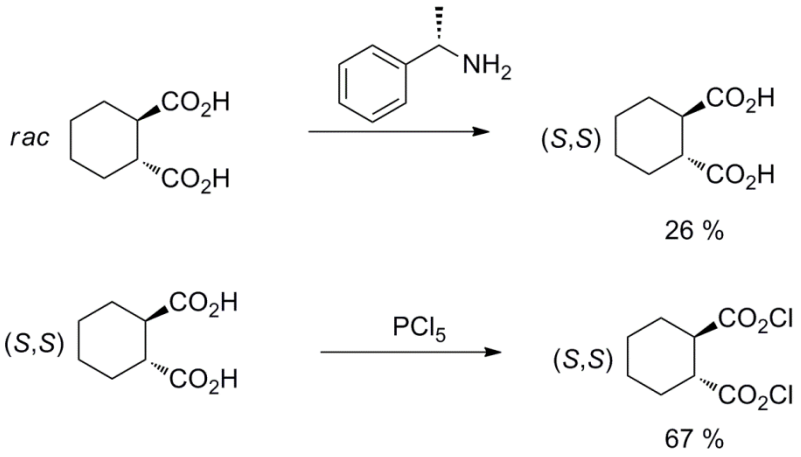
Table 7. Chiral absorption test of chiral crosslinked oligostyrene.

	Run[1]	Tröger's base	Flavanone
rac-Polystyrene	1	0.24(-)	1.81(-)
Chiral crosslinked oligostyrene[2]	2	1.31(+)	0.27(-)
Chiral crosslinked oligostyrene[2]	3	0.26(+)	0.53(-)

[1] Test conditions: racemic compound = 2.5 mg, hexane/2-propanol (95:5, v/v) = 10 mL, polymer 2 g. [2] M_n 2,628 M_w/M_n 1.52 from (Δ,*S*,*S*)-**2**, crosslinker 8 %.

B.1.2.5. Crosslinking using chiral crosslinker

A chiral crosslinker was introduced to induce a secondary helical structure into polystyrene. The chiral crosslinker was synthesized by resolving *rac-trans*-cyclohexane-1,2-dicarboxylic acid with (*S*)-1-phenylethylamine and transformation od (*S*,*S*)-*trans*-cyclohexane-1,2-dicarboxylic acid to acid chloride using PCl_5.



Scheme 4. Synthesis of a chiral crosslinker.

(*S*,*S*)-*trans*-cyclohexane-1,2-dicarbonyl chloride was used as chiral crosslinker.[36-37] Chiral polystyrene was also crosslinked using chiral crosslinker and aluminium trichloride instead of zinc chloride. ^{1}H NMR spectra of solvent swollen polystyrenes show broadening of peaks as in the case of achiral crosslinked polystyrenes. Chiral oligostyrenes were crosslinked using chiral crosslinker. 2 % crosslinked oligostyrene is optically active and its sign is reversed. Optical activities cannot be measured when more than 4 % crosslinker is used because it is insoluble in chloroform.

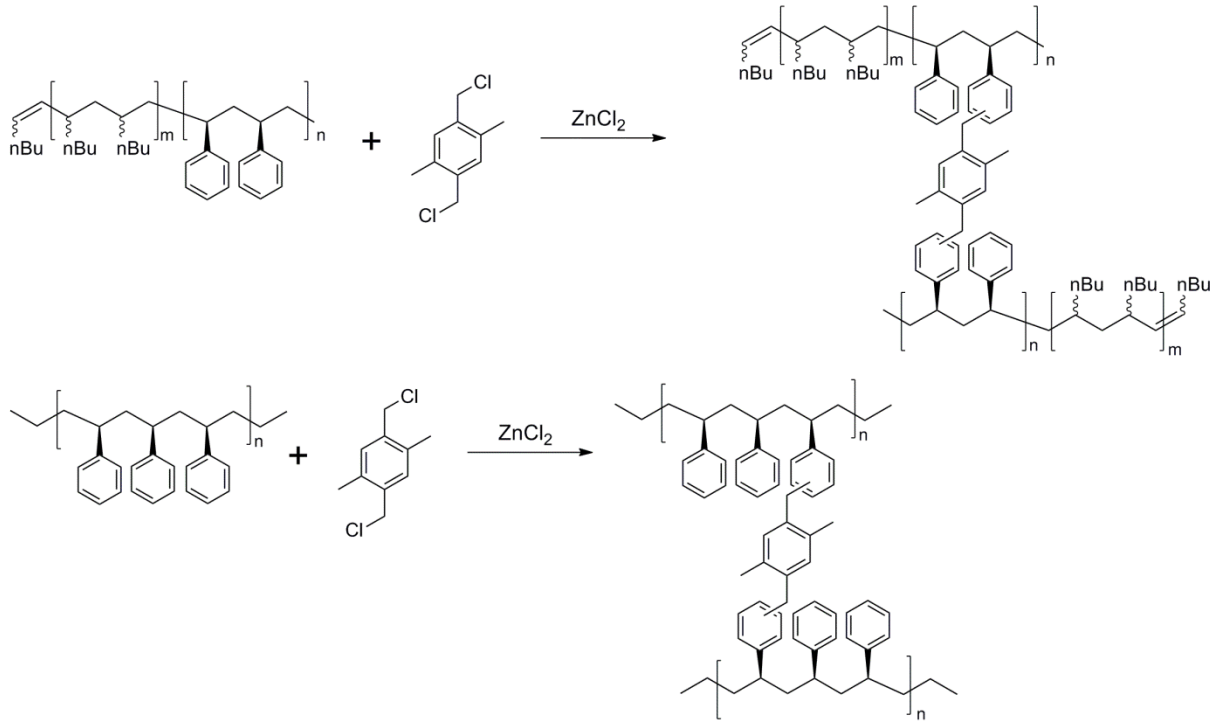
Table 8. Chiral crosslinked oligostyrenes using chiral crosslinker.

M_n	M_w/M_n	Crosslinker (mol%)	$[\alpha]^{23}_D$
2,118[1]	1.31	0	+1.5
2,224	1.37	2	-1.3
2,561	2.02	4	-
4,334	2.18	6	-

[1] Non-crosslinked oligostyrene was prepared. [styrene] = 1.6 mol/L, [1-hexene] = 2.3 mol/L, (Δ,*S*,*S*)-**1** = 2.5 μmol, [MAO] / [(Δ,*S*,*S*)-**2**] = 1800, toluene = 12 mL, *T* = 40 °C, *t* = 2 h.

B.1.3. Concluding Remarks

Chiral isotactic polystyrene was slightly crosslinked using 1,4-bis(chloromethyl)-2,5-dimethylbenzene to form a microgel. Crosslinking was done in solution or suspension medium using 1,4-bis(chloromethyl)-2,5-dimethylbenzene to form a microgel. Chiral isotactic crosslinked polystyrene can be used as material for column chromatography due to the pores produced by crosslinking. The peaks of crosslinker were characterized by ^{1}H and ^{13}C NMR spectroscopy. Crosslinked chiral oligostyrenes are optically active and its specific rotations vary depending on the degree of crosslinking. The chiral recognition ability of crosslinked chiral oligostyrene was investigated, but oligostyrenes do not show chiral recognition ability.



B.1.4. Experimental Section

Materials

All manipulations and reactions were performed under dry argon atmosphere using standard Schlenk tube and glove box techniques. Commercially available 1,4-bis(chloromethyl)-2,5-dimethylbenzene (Alfa Aesar), nitrobenzene (Alfa Aesar), zinc chloride (Merck), diethylzinc (Aldrich), methylaluminoxane (Aldrich) were used as received. 1-hexene (Aldrich), styrene (Fluka) were dried over calcium hydride and distilled under argon. Toluene was purified by use of a MBRAUN SPS-800 solvent purification system and degassed before use. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H 400.1 MHz, ^{13}C 125.6 MHz) at 25˚C. The specific rotation was measured in chloroform (λ = 589 nm at 23 °C) in a 1.0-dm measuring cell using a Jasco P-2000 polarimeter. GPC measurements were performed on an Agilent 1100 series instrument with a UV detector, using THF as solvent and polystyrene standards. Dynamic light scattering measurements were performed on a standard ALV 5000 system with a laser of 633 nm wavelength.

Polymerization using diethylzinc as a chain transfer agent

Homochiral isotactic oligostyrenes using diethylzinc as a chain transfer agent were prepared according to a literature procedure.[6-7] A Schlenk tube was charged with toluene (calculated for a total volume of 15 mL), 1.2 mL of a MAO solution in toluene (10 wt %; Aldrich), as well as the appropriate amount of diethylzinc and styrene. This mixture was stirred for 20 min at 40 °C, followed by addition of 0.5 mL of a 0.25 μM stock solution of the enantiomerically pure complex (*Δ*,*S*,*S*)-**1**, (*Δ*,*S*,*S*)-**2** or (*Λ*,*R*,*R*)-**2**. The reaction mixture was stirred at 40 ˚C for 24 h and then quenched by adding 0.5 mL of isopropanol; the polymer was precipitated from 100 mL of acidified methanol. The product was redissolved in chloroform and precipitated again from acidified methanol. This procedure was repeated. The oligomers were dried at 50 °C under vacuum for several hours.

Isotactic polymerization using 1-hexene as a chain transfer agent

Homochiral isotactic oligostyrenes with oligo(1-hexene) terminal groups were prepared according to literature procedure.[8] A Schlenk tube was charged with toluene (calculated for a total volume of 15 mL), 1.2 mL of a MAO solution in toluene (10 wt %; Aldrich), and a mixture of styrene and 1-hexene. This mixture was stirred for 20 min at 40 °C, followed by

addition of 0.5 mL of a 0.25 µM stock solution of the enantiomerically pure complex (*Δ*,*S*,*S*)-**1**, (*Δ*,*S*,*S*)-**2** or (*Λ*,*R*,*R*)-**2**. The reaction mixture was stirred at 40 °C for 2 h, quenched by addition of 0.5 mL of isopropanol and the polymer was precipitated from 100 mL of acidified methanol. The product was redissolved in chloroform and precipitated again from acidified methanol. This procedure was repeated. The oligomers were dried at 50 °C under vacuum for several hours.

Preparation of crosslinked isotactic polystyrene

To a solution containing 0.15 g (1.43 mmol of monomer unit) of isotactic polystyrene (M_n 116,210, M_w/M_n = 2.21) in 1.05 mL nitrobenzene, 5.8 mg (0.02 eq.) 1,4-bis(chloromethyl)-2,5-dimethylbenzene and 5 mg zinc chloride were added. The mixture was heated to 60 °C for 7 h. A yellow gel formed was washed with acetone and water and subsequently extracted with chloroform in a soxhlet apparatus overnight. The polymer was dried at 50 °C under vacuum for several hours.

Suspension crosslinking reactions of isotactic polystyrene

A solution containing 0.15 g (1.43 mmol of monomer unit) of isotactic polystyrene (M_n 116,210, M_w/M_n = 2.21) in 1.05 mL nitrobenzene was dispersed in 3 mL silicon oil (AK 350, Wacker), 2.89 mg (0.01 eq.) 1,4-bis(chloromethyl)-2,5-dimethylbenzene and 5 mg zinc chloride were added. The mixture was heated at 60 °C for 7 h. The suspension was washed with hexane, acetone and water. It was washed with acetone and water and subsequently extracted with chloroform in a soxhlet apparatus overnight. The polymer was dried at 50 °C under vacuum for several hours.

Preparation of crosslinked reactions of isotactic oligostyrene

To a solution containing 0.15 g (1.43 mmol of monomer unit) of isotactic polystyrene (M_n 116,210, M_w/M_n 2.21) in 1.05 mL nitrobenzene, the appropriate amount of 1,4-bis(chloromethyl)-2,5-dimethylbenzene and 5 mg zinc chloride were added. The mixture was heated at 60 °C for 4 h. The yellow solution was poured into acidified methanol in order to precipitate the crosslinked oligomer. The resulting colorless solid was filtered and was dissolved in chloroform and precipitated in acidified methanol. The oligomer was redissolved in chloroform and precipitated again into acidified methanol. After filtration and washing with methanol it was dried overnight at 50 °C under vacuum.

(*S*,*S*)-*trans*-1,2-dicarboxylic acid[36]

To a solution of (*S*)-1-phenylethylamine (0.70 g, 5.8 mmol) in EtOH (10 mL), racemic *trans*-1,2-dicarboxylic acid (1 g, 5.8 mmol) was added at room temperature. The mixture first became clear, and then a white solid formed. Toluene (10 mL) was added after the mixture was stirred for another 3 h, and the reaction mixture was brought to reflux until the solid was completely dissolved. The solution was cooled, and colorless crystals precipitated that were recrystallized twice from hot EtOH/toluene (1:1). The product obtained was dissolved in 1 mol/L conc. HCl, and extracted three times with Et_2O. The combined organic phase was dried over anhydrous sodium sulfate and filtered. Et_2O was evaporated under reduced pressure, affording the enantimerically pure (*S*,*S*)-1,2-cyclohexanedicarboxylic acid as colorless crystals (0.195 g, yield 27 %): $[\alpha]^{23}_D$ = +18.9 (*c* 0.98, acetone), lit. $[\alpha]^{20}_D$ = +18.3 (*c* 1.03, acetone)

(*S*,*S*)-Cyclohexane-1,2-dicarbonyl chloride[36]

(*S*,*S*)-*trans*-1,2-dicarboxylic acid (0.099 g, 0.512 mmol) and phosphorus pentachloride (0.238 g, 1.02 mmol) were stirred without solvent overnight at room temperature. After removing phosphorus oxychloride under vacuum**,** the residue was diluted with hexane, washed with cold water and brine, dried over anhydrous $MgSO_4$, and filtered. Product (91 mg, 85 %) was obtained as colorless oil by concentration of the filtrate and used for the crosslinking reaction without further purification: $[\alpha]^{23}_D$ = -12.5 (*c* 1.01, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.35-1.50 (m, 4H), 1.89-1.96 (m, 2H), 2.39-2.42 (m, 2H), 3.04-3.12 (m, 2H).

Preparation of crosslinked reactions of isotactic oligostyrene using a chiral crosslinker

To a solution containing 0.1 g (0.96 mmole of monomer unit) of isotactic polystyrene (M_n 2,118, M_w/M_n 1.31) in 1.05 mL nitrobenzene, the appropriate amount of (*S*,*S*)-*trans*-1,2-dicarboxylic acid and aluminium chloride (12 mg, 0.096 mmol) were added. The mixture was heated to 80 °C for 12 h. The brown solution was poured into acidified methanol in order to precipitate the crosslinked oligomer. The resulting solid was filtered off and dissolved in chloroform and then precipitated in acidified methanol. The oligomer was redissolved in chloroform and again precipitated into acidified methanol. After filtration and washing with methanol it was dried overnight at 50 °C under vacuum.

Chiral absorption test

A hexane/2-propanol mixture (95:5, v/v) was added to finely ground polymer (2.0 g) to wash the polymer prior to the chiral absorption experiment and the supernatant washing solution was removed with a syringe after standing at room temperature for 30 min. After the washing process was repeated three times, the polymer was dried under reduced pressure. A solution of racemic compound in a hexane/2-propanol mixture (10 mL, c = 0.5 g/L) was added to the polymer and the mixture was permitted to stand for 3 h with the vial tightly capped. An aliquot of the supernatant solution was then sampled and analyzed using a chiral HPLC system.

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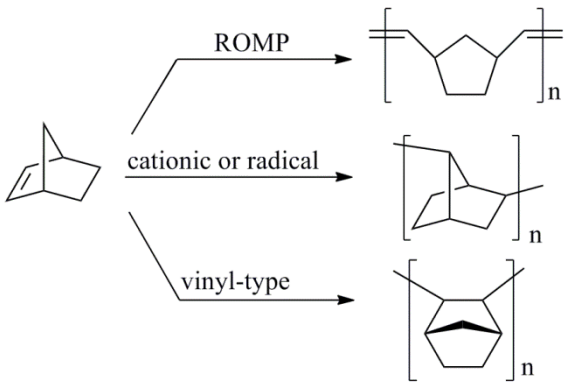
B.2. Optically Active Polynorbornene

B.2.1. Introduction

It is well known that norbornene can be homopolymerized by ring-opening metathesis polymerization (ROMP), cationic polymerization and addition polymerization.[1-6] Vinyl-type polymerization of norbornene gives rise to the formation of linked strained rings, which exhibit excellent dielectric properties, optical transparency, chemical resistance, and mechanical properties with respect to acyclic polymeric structures.[7-9] Chiral single site catalyst precursors provide an opportunity to prepare new chiral polymers. Even if most high molecular-weight stereoregular vinyl polymers with configurationally controlled stereocenters in the main chain can be prepared from prochiral olefins, they cannot show optically activities, because they contain an internal plane of symmetry.[10-11] On the other hand, low molecular-weight polyolefins can be optically active, provided significant asymmetric induction is achieved in the main chain.[12-13] However, optically active polymers can be obtained because of their tendency to form helices.[14-17] It is known that the erythro diisotactic isomer of polynorbornene has a rigid-rod helical conformation.[18-20] In this chapter, optically active polynorbornene is produced using an enantiopure (OSSO)-type catalyst.



Scheme 1. Schematic representation of the three different types of polymerization for norbornene.

B.2.2. Results and Discussion

B.2.2.1. Polymerization of Norbornene

Norbornene polymerization with *rac*-**1** was carried out using anilinium borate as an activator. The analog Ti(IV) dichloro complex is inactive for norbornene polymerization but *rac*-**1** is active probably due to larger size of the active center. Values for the conversion (M_n, and M_w / M_n) are reported in Table 1. Under the conditions employed, high conversion was achieved. Polynorbornene arising from *rac*-**1**/anilinium borate possesses a narrow molecular weight distribution. Molecular weights were measured up to 21,000 g/mol due to low solubility of polynorbornene in THF. Polynorbornene is soluble in chlorinated solvents (chloroform, dichlorobenzene, chlorobenzene) and toluene. The ^{1}H and ^{13}C NMR spectra for polynorbornene are presented in Figure 2. These polymerizations are vinyl addition in nature since no olefinic resonances are observed in the ^{1}H NMR spectra. ^{13}C NMR spectra show that polynorbornenes are *exo* enchained; the spectra do not exhibit resonances in the 20-24 ppm region considered as evidence of *endo* enchainment on the basis of model studies.[21-22] ^{13}C NMR spectra were measured but the tacticity was not determined because solution characterization by NMR was hampered by the insolubility of the polymer even at elevated temperature. The insoluble polymers are thought to be semi-crystalline due to a certain stereoregularity.[9] Since the glass transition temperatures of polynorbornenes should be very close to decomposition, it is difficult to determine them correctly.[23-24] Differential scanning calorimetry (DSC) studies did not show any melting transition up to 400 °C under a nitrogen atmosphere.

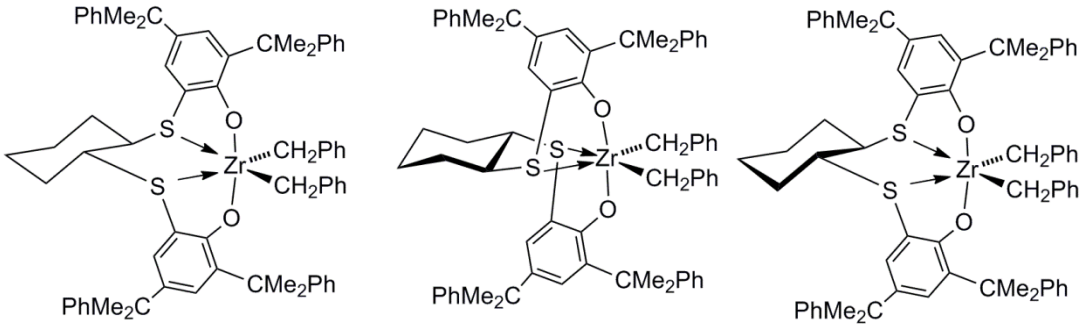


Figure 1. Structures of zirconium catalysts used for polymerization of norbornene.

Table 1. Polymerization of norbornene using *rac*-**1**.

Run	NB (mmol)	Cat (μmol)	NB/Cat	*T* (°C)	*t* (h)	Conversion (%)	M_n	M_w/M_n
1	3.8	10	380	25	1	77	N.D.[1]	N.D.
2	3.8	10	380	25	2	96	N.D.	N.D.
3	3.8	10	380	40	2	97	N.D.	N.D.
4	1.9	10	190	25	3	99	N.D.	N.D.
5	1.52	20	76	25	3	99	20,699	1.13
6	0.76	10	76	25	3	44	8,373	1.48
7	0.76	20	38	25	3	84	9,932	1,49
8	0.38	20	19	25	3	70	7,716	1.33

[1] N.D. = Not determined. Polymerization conditions:10 μmol *rac*-**1**, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$.

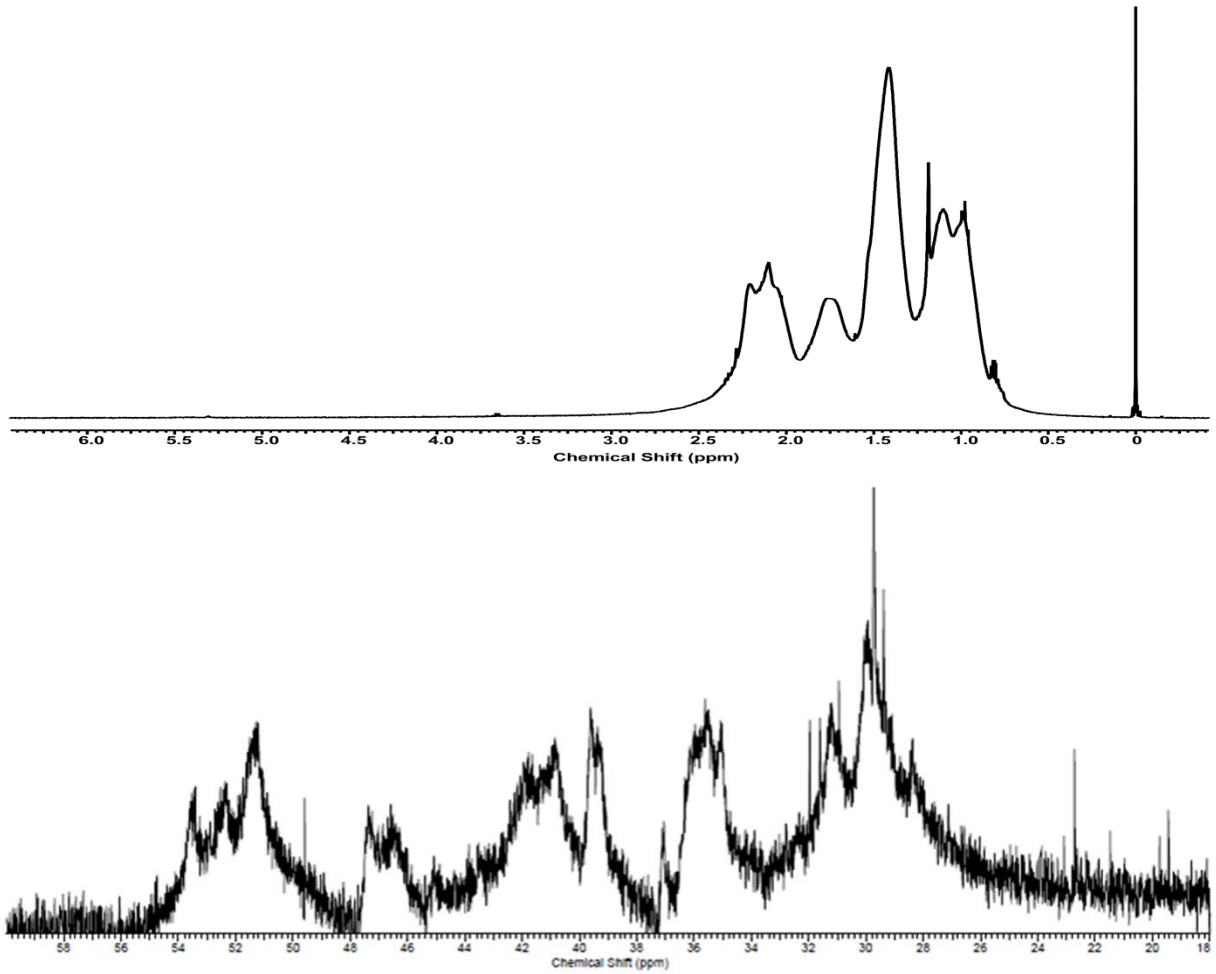
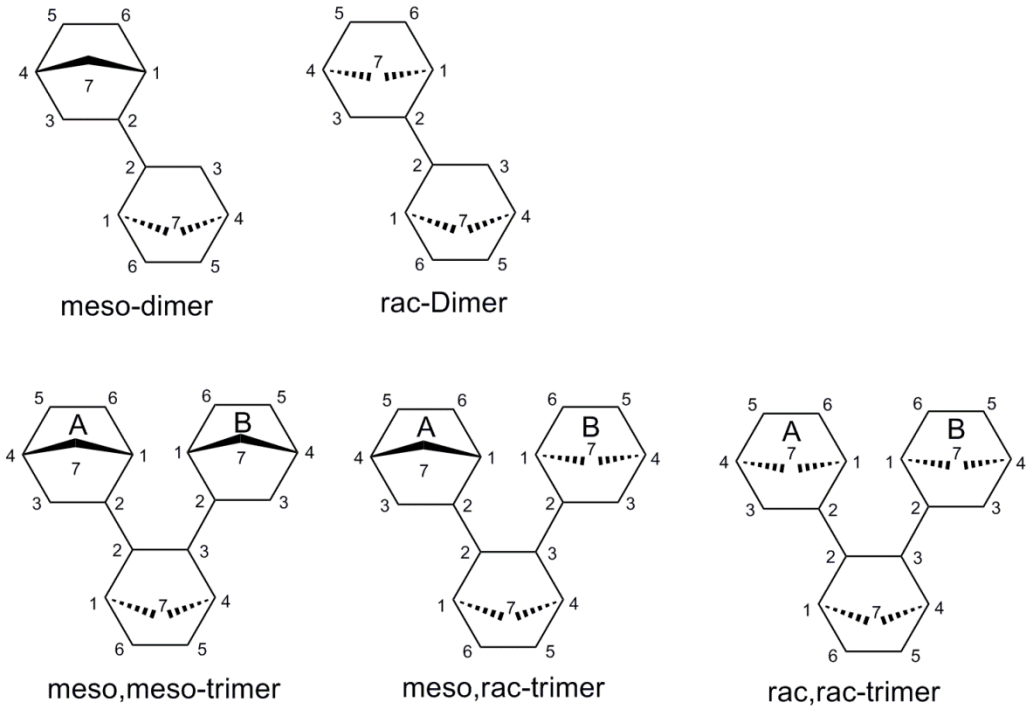


Figure 2. ^1H and ^{13}C NMR spectrum of polynorbornene in $CDCl_3$ at 25 °C.

B.2.2.2. Hydrooligomerization of Norbornene

Due to low solubility of polynorbornene in common organic solvents, hydrooligomerization reaction is conducted to elucidate its stereochemistry.[25-26] The Hydrodimers and hydrotrimers were separated by vacuum distillation and analyzed by NMR spectroscopy. Arndt et al. conducted hydrooligomerization and separated norbornene dimers and trimers.[25] ^{13}C NMR assignments of dimers are recorded in Table 2. Distributions of the hydrodimers and hydrotrimers of norbornene were calculated by integration of ^{13}C NMR peaks. Hydrodimers and hydrotrimers are also analyzed by GC/MS and the relative area of each peak is consistent with the integration of the ^{13}C NMR peak. The distributions of hydrodimers and hydrotrimers produced by catalyst *rac*-**1** are compared with results by Kaminsky.



Scheme 2. Structure of the norbornene hydrodimers and trimers.

Table 2. ^{13}C NMR chemical assignments of the norbornene hydrodimers.

meso-Dimer			*rac*-Dimer		
Signal	Chem. Shift	Assignment	Signal	Chem. Shift	Assignment
1a	48.74	C3	2a	48.25	C3
1b	38.53	C4	2b	40.81	C4
1c	38.23	C2	2c	36.77	C2
1d	37.19	C1	2d	36.14	C1

1e	35.07	C7	2e	35.64	C7
1f	30.71	C5	2f	30.41	C5
1g	29.05	C6	2g	29.16	C6

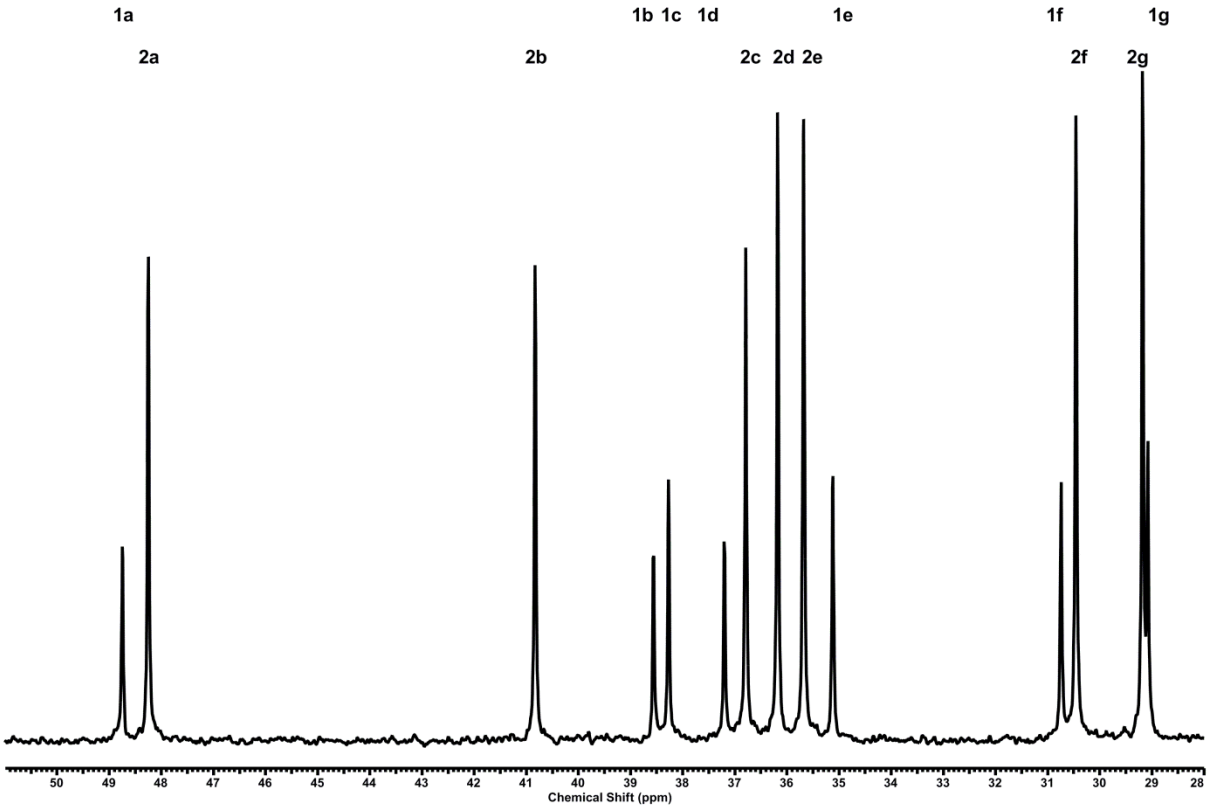


Figure 3. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of a mixture of the diastereomeric hydrodimers (1 = meso, 2 = racemic) of norbornene produced by *rac*-**1**.

Table 3. ^{13}C NMR chemical assignments of the tactic norbornene hydrotrimers. The indices a and b correspond to the *exo*-2-norbornyl groups.

meso,meso-Trimer			rac,rac-Trimer		
Chem. Shift	Apt	Assignment	Chem. Shift	Apt	Assignment
53.37	CH	C2,C3	54.71	CH	C2,C3
43.53	CH	C1a,C1b	42.59	CH	C2a,C2b
41.67	CH	C2a,C2b	41.64	CH_2	C3a,C3b
39.03	CH	C1,C4	40.29	CH	C1,C4
37.84	CH_2	C3a,C3b	40.09	CH	C1a,C1b
36.75	CH	C4a,C4b	36.86	CH	C4a,C4b
36.00	CH_2	C7a,C7b	36.00	CH_2	C7a,C7b
33.82	CH_2	C7	34.30	CH_2	C7

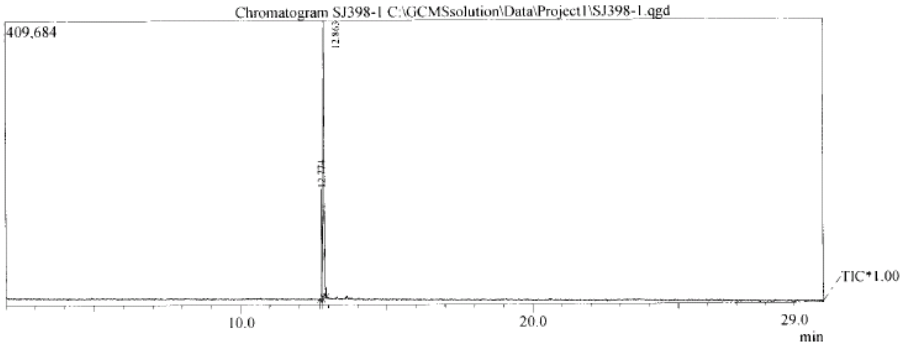
30.91	CH_2	C6a,C6b	31.13	CH_2	C6a,C6b
30.68	CH_2	C5,C6	30.86	CH_2	C5a,C5b
28.50	CH_2	C5a,C6b	29.46	CH_2	C5,C6

Table 4. ^{13}C NMR chemical assignments of the atactic norbornene hydrotrimers. The indices a (meso) and b (rac) correspond to the *exo*-2-norbornyl groups.

meso,rac-Trimer					
Chem. Shift	Apt	Assignment	Chem. Shift	Apt	Assignment
55.01	CH	C3	36.66	CH	C4a
53.28	CH	C2	36.43	CH_2	C7b
42.81	CH	C2a	35.74	CH_2	C7a
42.10	CH_2	C3b	34.12	CH_2	C7
41.91	CH	C2b	31.34	CH_2	C6b
41.87	CH	C1a	31.08	CH_2	C6a
39.62	CH	C4	30.91	CH_2	C6b
39.54	CH	C1	30.38	CH_2	C5a
38.79	CH	C1b	29.26	CH_2	C5
38.37	CH_2	C3a	28.42	CH_2	C6
36.78	CH	C4b			

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	12.774	12.713	12.808	386196	28.79	158456	28.38	2.44		E-1,5,9-Decatriene
2	12.863	12.808	12.925	955203	71.21	399897	71.62	2.39	V	E-1,5,9-Decatriene
				1341399	100.00	558353	100.00			



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	15.285	15.225	15.379	13348	6.99	2692	3.59	4.96		3-Chloro-1-cyclohexyldin
2	20.579	20.525	20.613	70440	36.91	30370	40.48	2.32		E-1,5,9-Decatriene
3	20.656	20.613	20.713	107042	56.09	41954	55.93	2.55	V	E-1,5,9-Decatriene
				190830	100.00	75016	100.00			

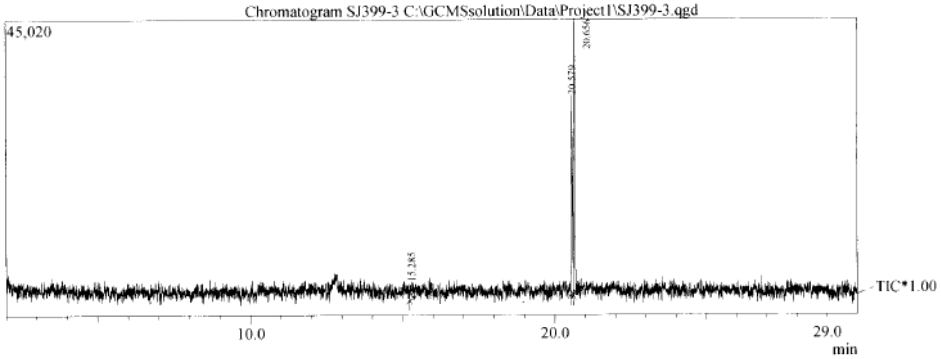


Figure 4. GC/ MS analysis of dimers (above) and trimers (below).

Both diastereomeric hydrodimers can be produced by a partially aspecific first insertion into the Zr-H bond. Aspecific first insertion into the Zr-H bond was proved by Pino et al[27-29] (Figure 5). This model shows that the methyl group of the propylene was placed in quadrant Q2 and the growing chain occupied quadrant Q1. Quadrant Q-1 and Q-2 were excluded because of the presence of the $–CH_2$-CH_2- bridge of the ligand. The stereoselectivity in α-olefins polymerization is connected both to the chirality of the catalytic center and to the position of the last monomeric unit of the growing chain with respect to the metal in the catalytic center. The absence of a growing chain in the Zr-H bond induced rather partially aspecific first insertion.

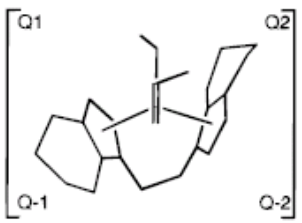


Figure 5. Pino's quadrant stereoselectivity model.

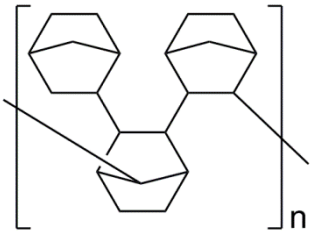
The C_2 symmetric *rac*-**1** produces only meso,meso and meso,racemic hydrotrimers indicating high stereospecificity of consecutive insertion. By using achiral Cp_2ZrCl_2 catalst, no racemic,racemic dimer is produced as a consequence of chain end control. In this case, the meso ratio of the hydrotrimers decreases compared to that of the hydrotrimers. The complex

rac-**1** shows an increased meso ratio compared to the C_2 symmetric rac-[$Me_2Si(Ind)$]$ZrCl_2$. It suggests that the third insertion of norbornene monomer is mainly isotactic.

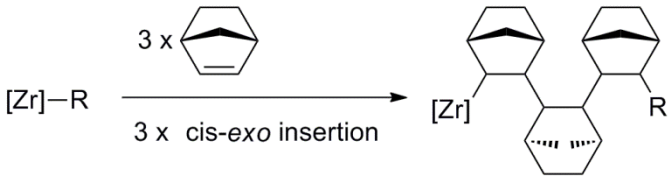
Table 5. Distributions of the hydrodimers and hydrotrimers produced by *rac*-**1** and different metallocene precursors.

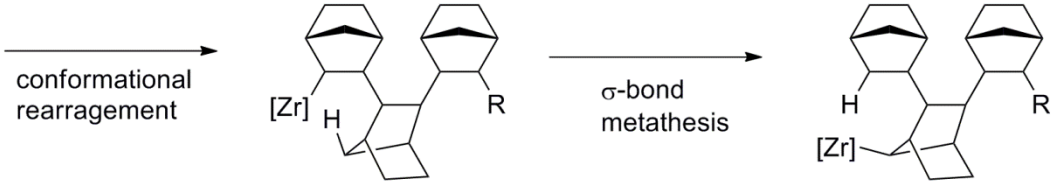
Catalyst	*T* (°C)	Hydrodimers		Hydrotrimers				
		meso (%)	rac (%)	mm (%)	mr (%)	rr (%)	meso (%)	rac (%)
Cp_2ZrCl_2	30	65	35	23	72	0	62	38
$[Ph_2C(Flu)(Cp)]ZrCl_2$	30	53	47	7.5	15	77.5	15	85
rac-[$Me_2Si(Ind)$]$ZrCl_2$	30	58	42	38	62	0	69	31
rac-**1**	25	27	73	40	60	0	70	30
rac-**1** (Deuteriooligomers)	25	31	69	42	58	0	71	29

Recent studies on the structure of norbornene oligomers obtained with rac-[$iPr(Ind)_2$]$ZrCl_2$-MAO (Ind = indenyl) suggested that polynorbornene has regular meso- and 2-exo,7'-syn-linked structural elements (Scheme 3, 4).[30-31] Porri et al. reported a 2,3-exo-disyndiotactic heptamer without C7 linkage using a $TiCl_4/AlEt_2Cl$ catalyst system. It is known that σ-metathesis is less frequent in titanium catalysts than zirconium catalysts.[32] Even if a pentamer isolated by Arndt et al. has no C7 linkage, no specific data were reported.[33] Thus there is no clear evidence whether 2,3-diisotactic polynorbornene without C7 linkage can be obtained. Deuteriooligomerization was conducted to investigate the structure of polynorbornene by checking the termination position. Deuteriooligomerization is conducted in the same way as hydrooligomerization and deuteriodimers and deuteriotrimers are isolated by vacuum distillation.

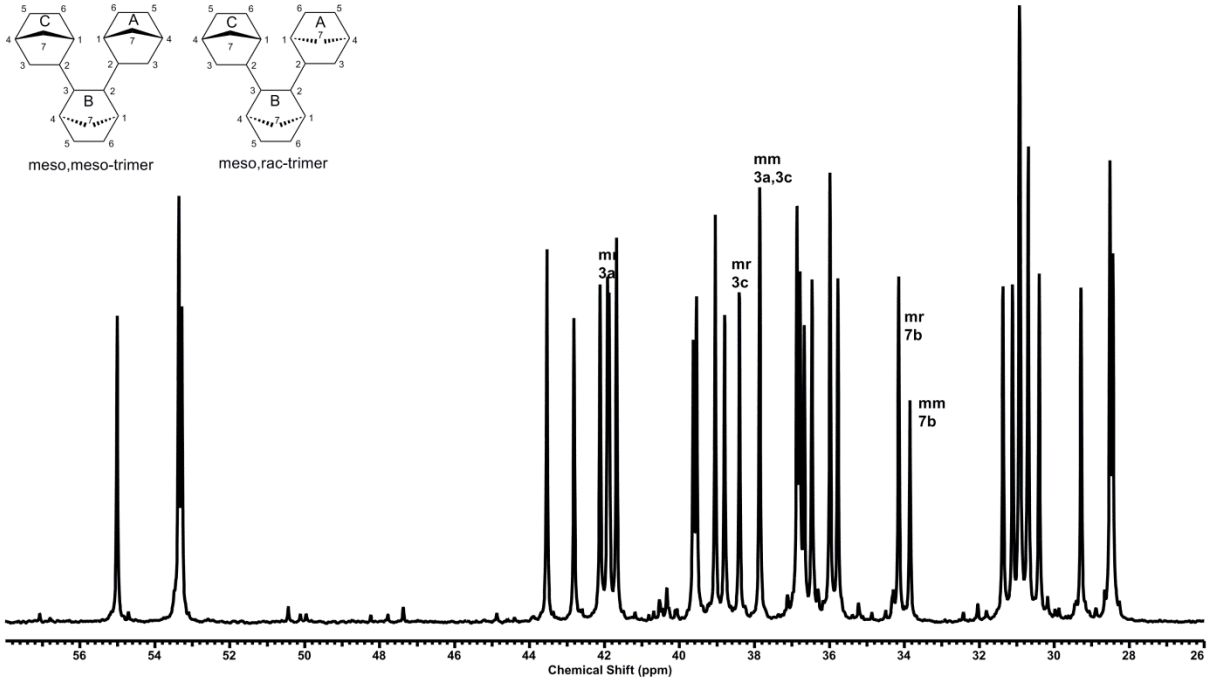


Scheme 3. Structure of a Polynorbornene derived from vinyl insertion and σ-bond methathesis.





Scheme 4. σ-Bond metathesis during the norbornene polymerization. R = H or D, CH_3, polymer, [Zr] = rac-[iPr(Ind)2Zr)$^+$; Ind = indenyl



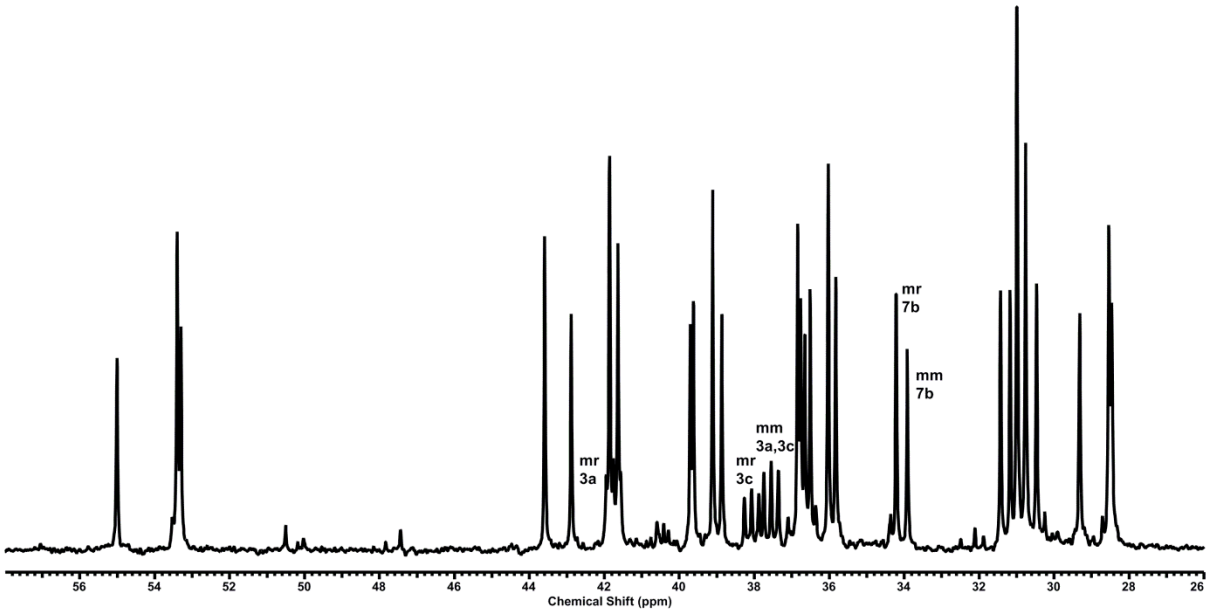


Figure 6. ^{13}C NMR spectra ($CDCl_3$, 25 °C) of the meso,meso and meso,racemic norbornene hydrotrimer generated with hydrogen (above) and deuterium (below).

The ^{13}C NMR spectrum of deuteriotrimers is compared with that of hydrotrimers. The resonance for the carbon atom C3a,c of the meso,meso trimer at δ= 37.86 ppm, for the carbon atom C3c at δ= 38.41 ppm and of the carbon atom C3a at 42.12 ppm from meso,racemic trimer have almost disappeared in the deuterated compound and a new signal with the characteristic 1:1:1 triplet of a carbon atom bound to deuterium is observed. The resonance of the bridging carbon atom C7 from meso,meso trimer at δ = 33.92 and for the bridging carbon atom C7 from meso,racemic trimer at δ = 34.22 ppm from have remained intact. These results suggest that polynorbornene produced by *rac*-**1** contains no C7 linkage.

The insoluble fraction of hydrooligomers and deuteriooligoemers in diethylether was analyzed by ^{13}C NMR spectroscopy. A spectrum of the insoluble fraction of hydrooligomers in $CDCl_3$ shows 13 carbon peaks with same intensity and one peak with twice the intensity as any other of the 13 peaks. It is assumed that this compound has 14 carbon peaks and can be a tetramer. Since the chemical shift of the peak at δ= 53.55 ppm is similar to 53.37 ppm due to the C2, C3 carbon atom from the meso, meso trimer, it can be considered a meso,meso,meso tetramer. The signal at δ= 35.07 ppm of the carbon atom has almost disappeared in the deuterated compound and new triplet signal is observed. But the signal at δ = 34.14 ppm which should be from the carbon atom C7 has remained intact. Thus only one termination position is deuterated, which suggests that norbornene is oligomerized without C7 linkage in the tetramer as in the trimer.

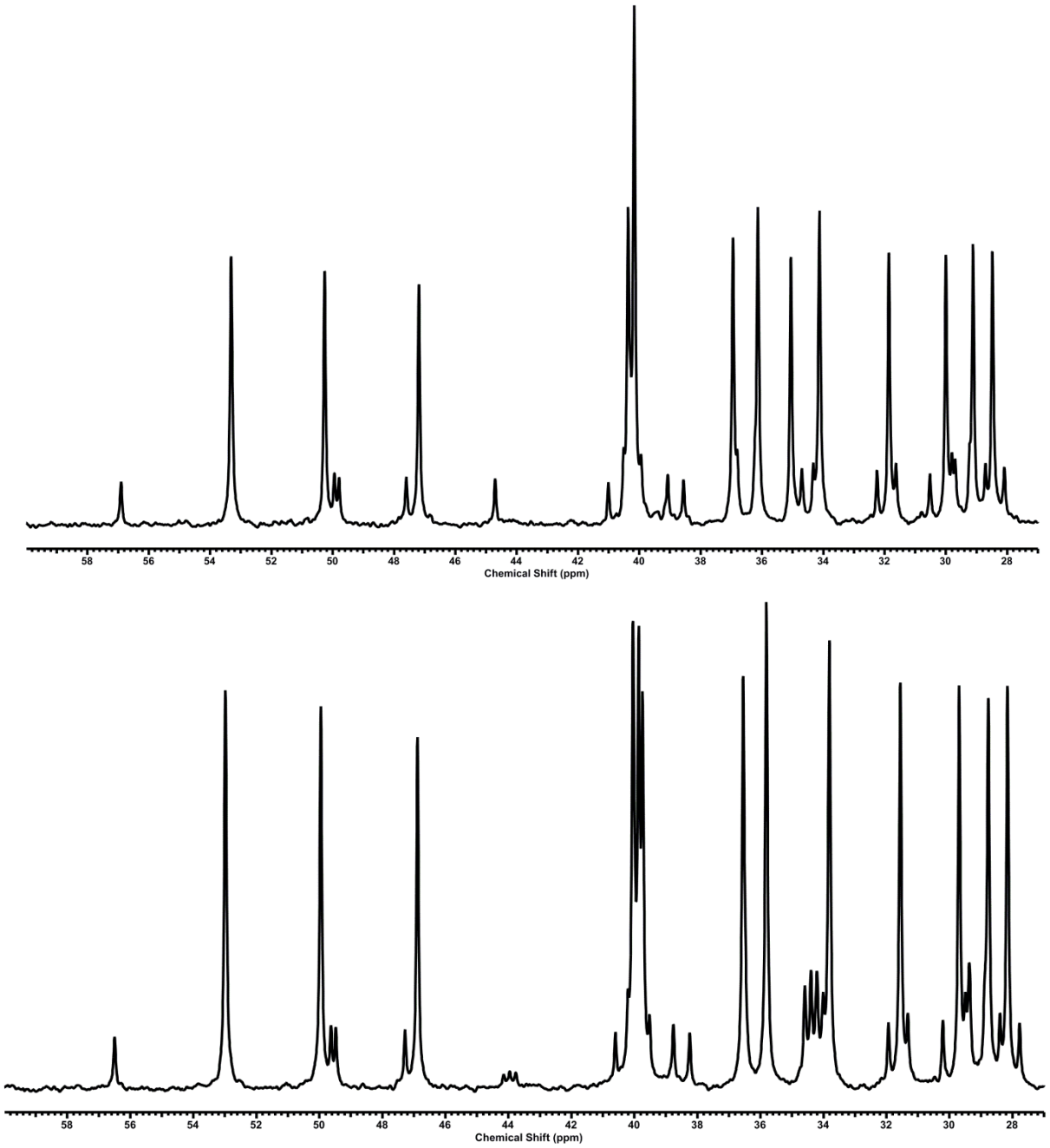


Figure 7. ^{13}C NMR spectra of the diethylether insoluble fraction of norbornene hydrooligomers generated with hydrogen (above) and deuterium (below) in $CDCl_3$.

Recrystallization of the ether insoluble fraction in toluene gave needle-shaped single crystals. Single crystal X-ray crystallography indicated that the crystalline compound was indeed a meso,meso,meso tetramer (mp 204 °C, m/z = 378).

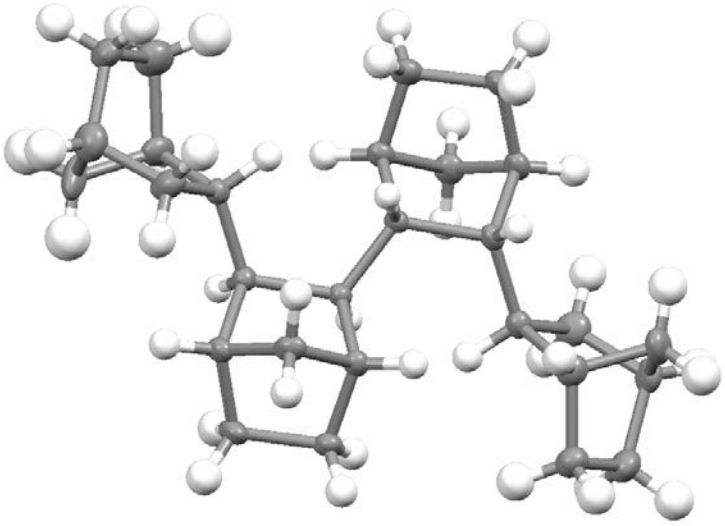


Figure 8. View of the molecular structure of the meso,meso,meso norbornene tetramer with anisotropic displacement parameters drawn at 50% probability level.

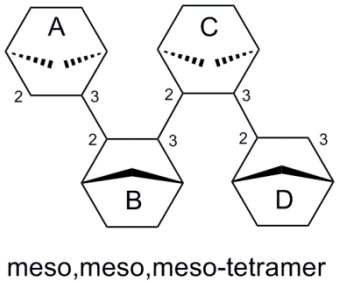


Figure 9. Labeling of meso,meso,meso tetramer.

Table 6. Selected bond lengths (Å) and torsion angles (°) defining the conformation of the norbornene tetramer. The monomer units are labeled with letters A to D.

	C2-C3	C3-C2'	C2°-C3°-C2-C3		C3°-C2-C3-C2'
A	1.558	1.563	A-B	122.70	A-B-C	12.58
B	1.597	1.522	B-C	179.22	B-C-D	-9.83
C	1.589	1.575	C-D	-119.41	-	-
D	1.570	-				

B.2.2.3. Polymerization of Norbornene Using Enantiopure Catalyst

According to previous studies, the erythro diisotactic isomer of polynorbornene has a rigid-rod helical conformation.[18-20] When the enantiopure catalyst is used, it is possible to induce an enantiomeric helix with a fixed screw sense. Polynorbornene was produced using enantiopure catalysts and their optical activities were measured. Even if polynorbornenes have a low solubility, their optical activity did not decrease below a concentration of 4 mg/mL in chlorobenzene and 1,2-dichlorobenzene.[34] Increasing the molecular weight from 9,800 to 16,000 does not decrease the optical rotations. This result suggests that optical activity of polynorbornene does not come from the terminal chiral group.

Table 7. Polymerization of norbornene obtained using enantiopure zirconium complexes.

Run	Catalyst	NB (mmol)	Cat (μmol)	NB/Cat	M_n	M_w/M_n	Conversion (%)
1	(Δ,*S*,*S*)-**1**	0.760	20	38	9,830	1.07	88
2	(Δ,*S*,*S*)-**1**	1.520	20	76	13,571	1.25	82
3	(Δ,*S*,*S*)-**1**	1.132	20	57	16,046	1.23	73
4	(Λ,*R*,*R*)-**1**	1.132	20	57	14,530	1.28	80
5	(Λ,*R*,*R*)-**1**	0.828	20	41	13,146	1.29	87

Polymerization conditions:10 μmol catalyst, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$.

Table 8. Optical rotations of polynorbornene obtained using enantiopure zirconium complexes.

Run	Chlorobenzene		1,2-dichlorobenzene	
	$[\alpha]_D$	c (mg/mL)	$[\alpha]_D$	c (mg/mL)
1	+20.5	4.0	+28.3	1.9
2	+28.4	4.0	+35.3	1.20
3	+30.5	4.0	+29.3	1.65
4	-31.6	4.0	-	-
	-29.8	2.0	-	-
5	-34.1	4.0	-	-
	-33.3	2.0	-	-

B.2.2.4. Copolymerization of Norbornene

Ethylene/norbornene copolymers display interesting properties like high heat/chemical resistance, excellent transparency and low double refraction. Since its amorphous nature makes it more soluble in organic solvents, microstructural characterization by ^{13}C NMR analysis can be performed.[35-38] Ethylene/norbornene copolymers produced by *rac*-**1** are low molecular weight polymers. These molecular norbornene/ethylene copolymers exhibit signals at 4.6-4.7 ppm in the ^{1}H NMR spectrum corresponding to vinylidene groups which result from 1,2-insertion and β-hydrogen elimination.[39]

Table 9. Copolymerization of norbornene with ethylene.

Run	NB (mmol)	C_2H_4 pressure (bar)	NB in polymer (%)	*t* (h)	*T* (°C)	NB conversion (%)	M_n	M_w/M_n
1	5.52	2	29	1	25	59	1,184	1.43

Polymerization conditions:10 μmol *rac*-**1**, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$.

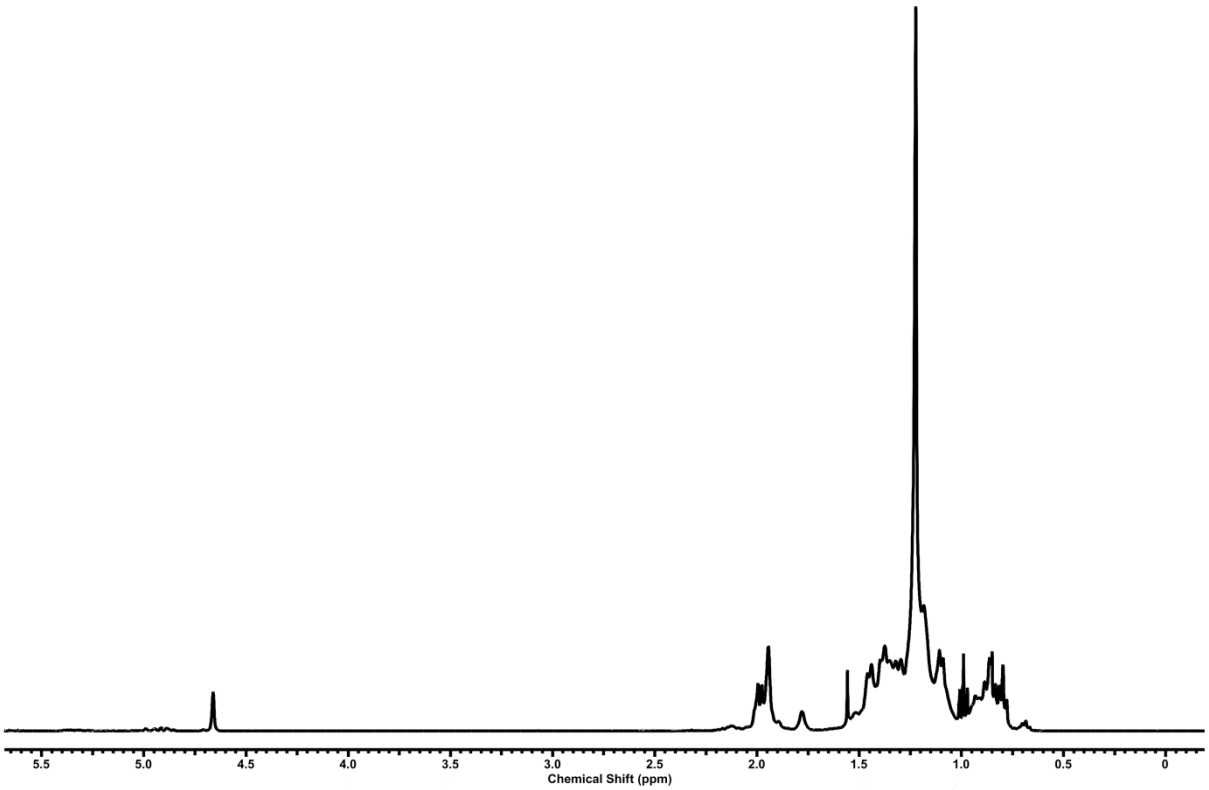
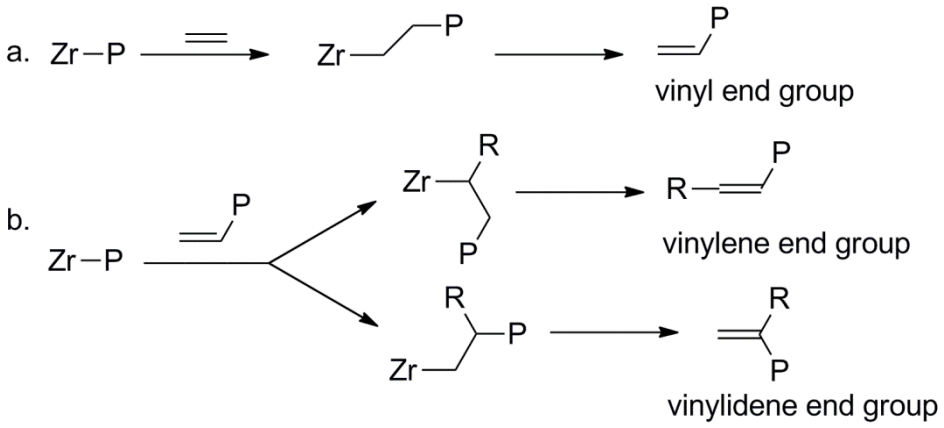


Figure 10. ^{1}H NMR spectrum of low molecular weight norbornene/ethylene copolymer in $CDCl_3$ at 25 °C.



Scheme 5. Mechanisms of 1-alkene termination.

Since polynorbornene is not melt-processable, its solubility is a prerequisite for any applications. It is reported that if alkyl derivatives of norbornene are polymerized, the melt processibility can be improved.[40-41] To overcome the low solubility of polynorbornene in standard organic solvents, 5-butyl-2-norbornene was synthesized and polymerized using *rac*-**1**.[42-43] *rac*-**1** is not active for 5-butyl-2-norbornene polymerization at room temperature and conversion is less than 25% even at elevated temperature. The produced polymer has low molecular weight and is optically inactive.

Table 10. Homopolymerization of 5-butyl-2-norbornene.

Run	Catalyst	5-butyl-2-norbornene (mmol)	*T* (°C)	Yield (mg)	Conversion (%)	M_n	M_w/M_n
1	*rac*-**1**	1.20	90	43	23	N.D.[1]	N.D.
2	*rac*-**1**	2.40	25	<10	-	N.D.	N.D.
3	(Δ,*S*,*S*)-**1**	2.40	90	75	20	1,002	1.05

[1] N.D. = Not determined. Polymerization conditions:10 μmol catalyst, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$.

5-Butyl-2-norbornene was copolymerized with norbornene using *rac*-**1**. The conversion increases compared to that of homopolymerization and the high molecular weight indicates that the product is a polymer. The Copolymer possesses narrow molecular weight distributions and a single peak in GPC indicates that it is a copolymer and not a mixture of homopolymers. Copolymers produced by chiral catalyst are still optically active and a concentration of 20 mg/mL is accessible for measurement of optical activity due to good

solubility in chloroform and other organic solvents. The ^{1}H NMR spectrum of the copolymer shows methyl peak of the butyl group and approximately 50% 5-butyl-2-norbornene are present in the material. The tacticity cannot be investigated because the existence of another chiral center in 5-butyl-2-norbornene makes the spectrum complicated and the solubility does not increase much.

Table 11. Copolymerization of 5-butyl-2-norbornene with norbornene.

Run	Catalyst	Norbornene (mmol)	5-Butyl-2-norbornene (mmol)	*T* (°C)	Conversion (%)	M_n	M_w/M_n	$[\alpha]_D$[1]
1	*rac*-**1**	1.38	2.41	90	50	22,402	1.20	-
2	(Δ,*S*,*S*)-**1**	1.38	1.38	90	44	13,164	1.74	+12.8

Polymerization conditions:10 μmol catalyst, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$. [1]20 mg/mL $CHCl_3$.

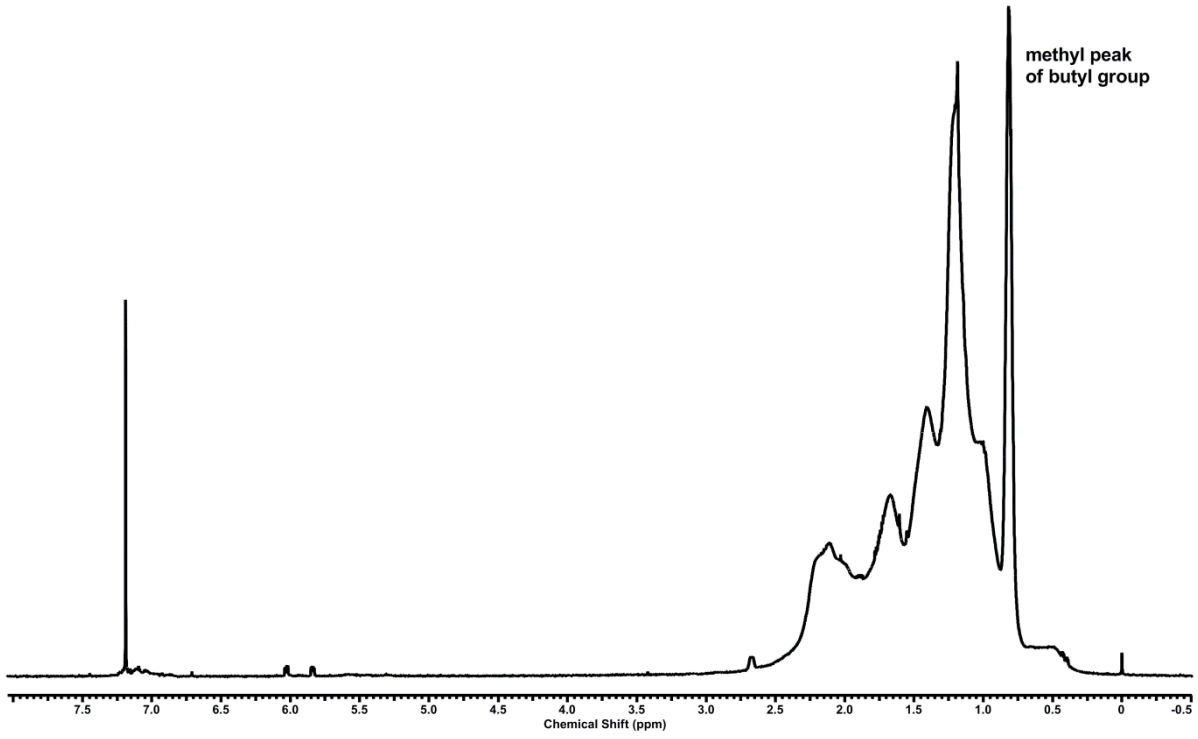


Figure 11. ^{1}H NMR spectrum of 5-butyl-2-norbornene/norbornene copolymer in $CDCl_3$ at 25 °C.

In another approach to increase the solubility of polynorbornene, norbornene was copolymerized with butadiene. The copolymer possesses narrow molecular weight distributions and a single peak in GPC indicates that it is a copolymer not a mixture of homopolymers. Complex *rac*-**1** is not active for butadiene/norbornene copolymerization at

room temperature but the conversion increases at 90°C. In the polymer, butadiene is enriched compared to the feed ratio of norbornene/butadiene suggesting that butadiene is polymerized more rapidly than norbornene. Even if copolymers are produced, their solubilities do not improved significantly and copolymer is only soluble in toluene, THF and chlorinated solvents as norbornene homopolymer. Copolymer produced by chiral catalyst is still optically active and a concentration of 20 mg/mL is accessible to measure the optical activity due to better solubility in chloroform and other organic solvents. Solution characterization by ^{13}C NMR is hampered by low concentration and the vinyl peaks of butadiene in ^{1}H NMR spectrum are similar to those of butadiene homopolymer. These observations suggest that the butadiene/norbornene copolymer has a rather blocky structure and its optical activity results from the polynorbornene segment of the copolymer and 1,2 addition product of polybutadiene. Due to the different reactivity between butadiene and norbornene, block copolymerization is conducted but polynorbornene or polybutadiene homopolymers are found.

Table 12. Copolymerization of norbornene with butadiene.

Run	Norborene (mmol)	Norbornene: butadiene (feed)	Norbornene: butadiene (polymer)	*t* (h)	*T* (°C)	Conversion (%)	M_n	M_w/M_n
1	2.21	65:35	N.D.[1]	2	25	0	N.D.	N.D.
2	2.21	65:35	N.D.	2	50	17	N.D.	N.D.
3	1.10	65:35	47:53	2	90	48	5,461	2.46
4	3.32	97:3	81:19	2	90	36	8,801	1.58
5	6.63	97:3	82:18	2	90	26	13,746	1.53
6	6.63	97:3	80:20	4	90	18	15,125	1.48
7	13.11	97:3	82:18	2	90	9.8	17,523	1.49
8	4.46	65:35	45:55	2	90	45	14,548	1.53

[1] N.D. = Not determined. Polymerization conditions:10 μmol *rac*-**1**, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$.

Table 13. Copolymerization of norbornene with butadiene using (Δ,*S*,*S*)-**1**.

.Run	Norborene (mmol)	Norbornene: butadiene (feed)	Norbornene: butadiene (polymer)	Conversion (%)	M_n	M_w/M_n
1	3.32	97:3	81:19	36	8,801	1.58
2	6.63	97:3	82:18	26	13,746	1.53
3	13.11	97:3	82:18	9.8	17,523	1.49
4	4.46	65:35	45:55	45	14,548	1.53

Polymerization conditions: *t* = 2 h, *T* = 90 °C, 10 μmol (Δ,*S*,*S*)-**1**, 1 eq. [$(Me_2NHPh)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$.

Table 14. Optical rotations of norbornene/butadiene copolymer using (Δ,*S*,*S*)-**1**.

Run	Chloroform	
	$[\alpha]_D$	c (mg/mL)
1	-4.5	10
	-6.6	20
2	-10.9	10
	-12.2	20
3	-13.9	10
	-11.4	20
4	-8.3	5.4
	-7.6	10
	-6.3	20

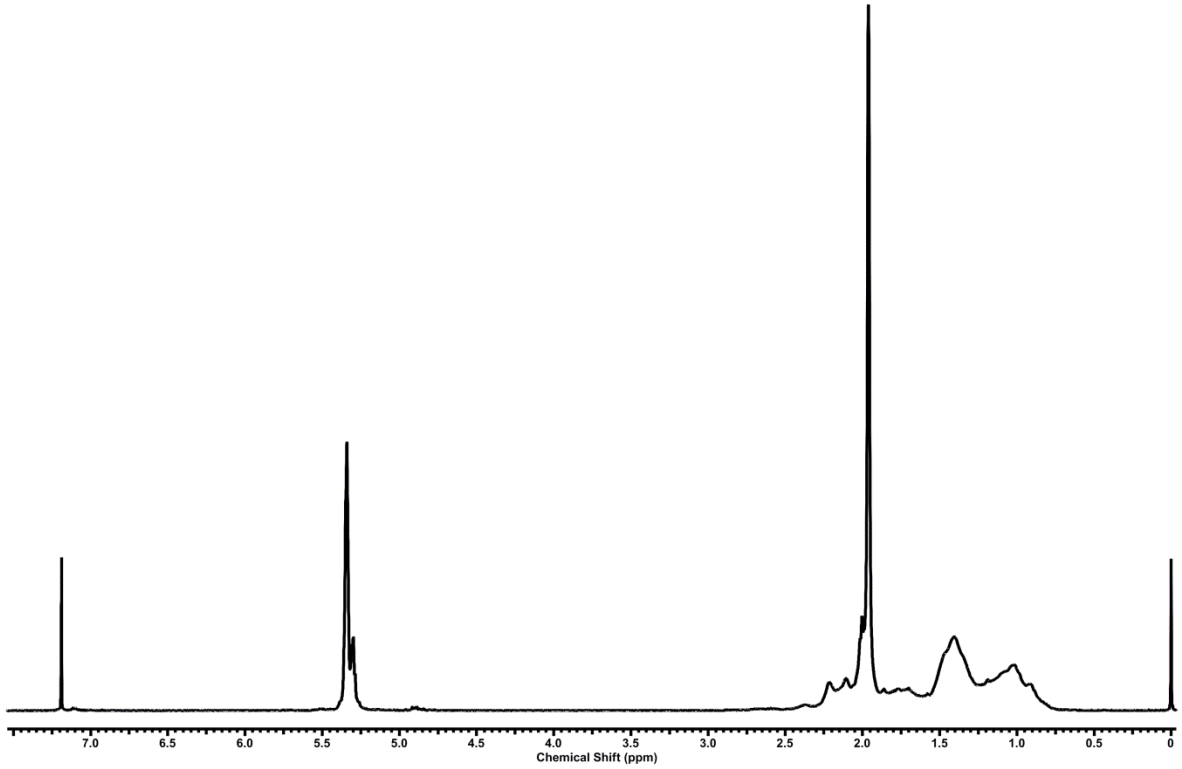
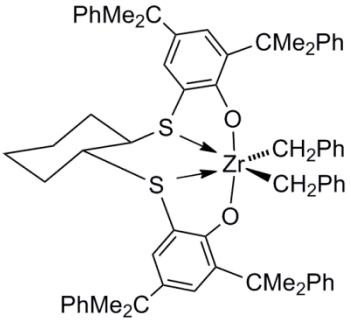


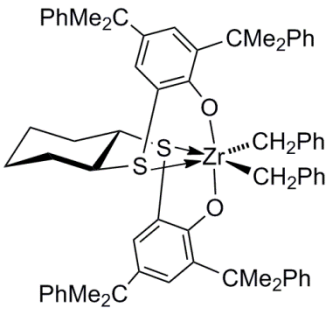
Figure 12. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of norbornene-butadiene copolymer.

B.2.3. Concluding Remarks

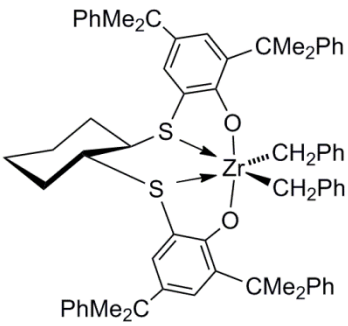
Polynorbornene was produced using racemic as well as enantiopure zirconium complexes with (OSSO)-type ligands. Polynorbornenes are addition polymers in nature and have narrow molecular weight distributions. To determine their tacticity, hydrooligomerization was performed. The C_2 symmetry of the zirconium complex is responsible for the diisotactic insertion. The termination position of deuteriooligomerizaion suggests that polynorbornene produced by *rac*-**1** has no C7 linkage. Optically active Polynorbornene was produced using enantiopure zirconium catalyst (Δ,*S*,*S*)-**1** and (Λ,*R*,*R*)-**1**. This result suggests that the optical activity of polynorbornene comes from helices with a fixed sense of rotation.



rac-**1**



(Δ,*S*,*S*)-**1**



(Λ,*R*,*R*)-**1**

B.2.4. Experimental Section

Synthesis of rac-dibenzyl-(dithiacyclohexanediyl-2,2'-bis(4,6-di-cumylphenolato))-zirconium

To a solution of 0.48 mmol $Zr(Bz)_4$ in 15 mL toluene, 0.48 mmol of proligand in 20 mL toluene were slowly added at -60 °C. The solution was allowed to warm to room temperature and was stirred for two further hours. After evaporating the solvents under vacuum washed with pentane, the product was obtained as yellow powder. (0.35 mmol, 73 %); ^{1}H NMR (C_6D_6): δ 0.55(m, 2 H, cyclohexyl), 1.08(m, 2 H, cyclohexyl), 1.12(d, $^2J_{HH}$ = 8.53 Hz, 2 H, ZrC*H*$_2$Ph), 1.24 (m, 2 H, cyclohexyl), 1.58(s, 6 H, C(C*H*$_3$)$_2$(C_6H_5)), 1.61 (s, 6 H, C(C*H*$_3$)$_2$(C_6H_5)), 1.65 (s, 6 H, C(C*H*$_3$)$_2$(C_6H_5)), 1.66 (s, 6 H, C(C*H*$_3$)$_2$(C_6H_5)), 1.71 (m, 2 H, cyclohexyl), 1.87(d, $^2J_{HH}$ = 8.53 Hz, 2 H, ZrC*H*$_2$Ph), 1.91 (m, 2 H, SC*H*), 6.41 (d, $^4J_{HH}$ = 7.28 Hz, 4 H, Zr-CH_2-C_6H_5-2-*H*), 6.82 (d, $^4J_{HH}$ = 2.01 Hz, 2 H, C_6H_2-3-*H*), 7.20-6.86 (m, 26 H, C(CH_3)$_2$(C_6H_5) and Zr$CH_2C_6H_5$), 7.50 (d, $^4J_{HH}$ = 2.01 Hz, 2 H, C_6H_2-5-*H*) ppm.

General procedure for norbornene polymerization

Norborene polymerizations were carried out as follows: To a flask equipped with a magnetic stirrer, toluene (7 mL), the precatalyst (10 μmol), [$PhNMe_2H$][$B(C_6F_5)_4$] (10 μmol), and 2 mL $AlOct_3$ (10 mM solution, 20 μmol) were added. The solution was kept stirring for 20 min at room temperature. The appropriate amount of norbornene was added via syringe. The polymerization was performed for the desired time. The reaction was quenched by adding 0.5 mL of isopropanol. The polymer was precipitated from acidified methanol and was dried under vacuum overnight.

Synthesis of norbornene hydrooligomers

Norbornene hydrooligomers were synthesized according to literature procedures.[25] A hot autoclave was evacuated and pressurized with argon several times. Toluene (90 mL), norbornene (10.0 g, 106 mmol), [$PhNMe_2H$][$B(C_6F_5)_4$] (50 μmol) and $AlOct_3$ (25 wt % in hexanes, 100 μmol) were mixed in a glove box and added. Hydrogen was pressurized to 5 bar under stirring to saturate the solution. After depressurizing, a solution of the catalyst (5 μM solution, 10 mL) was fed to the autoclave followed by re-pressurizing to 5 bar. After 20 h the pressure was released. 5 mL concentrated HCl in 50 ml distilled water was added and stirred for 30 min. The organic phase was isolated, washed with saturated Na_2CO_3 solution and dried

with Na_2SO_4. Solvent and norbornene were removed by distillation. The residue was vacuum distilled to isolate dimers and trimers.

Recrystallization of the meso,meso,meso norbornene tetramer

A distillation residue of hydrooligomers was washed with diethylether. The ether insoluble fraction was dissolved in hot toluene and recrystallized in toluene at room temperature. ^{13}C NMR (400 MHz, $CDCl_3$): δ 28.49 (CH_2), 29.12 (CH_2), 30.00 (CH_2), 31.86 (CH_2), 34.12 (CH_2), 35.05 (CH_2), 36.14 (CH_2), 36.95 (*C*H), 40.16 (*C*H), 40.37 (*C*H), 47.19 (*C*H), 50.27 (*C*H), 53.32 (*C*H). Mp 204 °C, EI MS: *m*/*z* (%) = 378 (21) [M^+], 283 (69) [M^+-C_7H_{10}], 201 (63) $[C_{15}H_{22}]^+$, 95 (92) $[C_7H_{11}]^+$, 67 (100) $[C_5H_8]^+$.

Ethylene/norbornene copolymerization

To an autoclave equipped with a magnetic stirrer, toluene (7 mL), the catalyst (10 μmol), $[PhNMe_2H][B(C_6F_5)_4]$ (10 μmol), and 2 ml $AlOct_3$ (10 mM solution, 20 μmol) were added in a glove box. The solution was kept stirring for 20 min at room temperature. Ethylene was pressurized to 3 bar under stirring to saturate the solution. After depressurizing, norbornene (2 mL, 2.8 M solution) was fed to the autoclave followed by re-pressurizing to 3 bar. The polymerization was carried on for 1 h. The reaction was quenched by adding 0.5 mL isopropanol. The polymer was precipitated from acidified methanol and was dried under vacuum overnight.

Synthesis of 5-butyl-2-norbornene

A 500 mL steel pressure vessel was charged under argon atmosphere with 26.4 g (0.2 mol) of dicyclopentadiene and 67.4 g (0.8 mol) of 1-hexene. The reaction mixture was heated to 200 °C for 10 h. The pressure increases up to 10 bar. After cooling to ambient temperature of the reaction mixture excess 1-hexene was removed by distillation. The product was isolated by fractionated distillation under vacuum. *endo*/*exo ratio* of product = 77/23 yield 6 %; ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.14 (*endo, exo* CH_3CH_2), 22.94 (*endo, exo* CH_3CH_2), 30.93 (*endo* $CH_3CH_2CH_2$), 31.12 (*exo* $CH_3CH_2CH_2$), 32.44 (*endo* $CH_3(CH_2)_2CH_2$), 33.10 (*exo* $CH_3(CH_2)_2CH_2$), 34.50 (*endo* $CH_2CH(CH_2)_3CH_3$), 36.30 (*exo* $CH_2CH(CH_2)_3CH_3$), 38.73(*endo, exo* $CH(CH_2)_3CH_3$), 41.86 (*exo* $CHCH_2CH(CH_2)_3CH_3$), 42.52 (*endo* $CHCH_2CH(CH_2)_3CH_3$), 41.86 (*exo* $CHCH(CH_2)_3CH_3$), 42.52 (*endo* $CHCH(CH_2)_3CH_3$), 45.20

(*exo* $CH_2CHCH(CH_2)_3CH_3$), 45.41 (*endo* $CH_2CHCH(CH_2)_3CH_3$), 46.35 (*exo* $CH_2CHCH(CH_2)_3CH_3$), 49.55 (*endo* $CH_2CHCH(CH_2)_3CH_3$), 132.45 (*endo* $CHCHCH(CH_2)_3CH_3$), 136.15 (*exo* $CHCHCH(CH_2)_3CH_3$), 136.83 (*endo* $CHCHCHCH(CH_2)_3CH_3$), 136.96 (*exo* $CHCHCHCH(CH_2)_3CH_3$).

5-Butyl-2-norbornene/norbornene copolymerization

To a flask equipped with a magnetic stirrer, toluene (7 mL), the catalyst (10 μmol), $[PhNMe_2H][B(C_6F_5)_4]$ (10 μmol), and 2 mL $AlOct_3$ (10 mM solution in toluene, 20 μmol) were added in a glove box. The solution was kept stirring for 20 min at room temperature. Norbornene (0.5 ml, 2.8 M solution) and 5-butyl-2-norbornene (0.20 g, 1.38 mmol) were premixed and was added by a syringe. The polymerization was carried on for 1 h. The reaction was quenched by adding 0.5 mL of isopropanol. The polymer was precipitated from acidified methanol and was dried under vacuum overnight.

Butadiene/norbornene copolymerization

To a flask equipped with a magnetic stirrer, toluene (7 mL), the catalyst (10 μmol), $[PhNMe_2H][B(C_6F_5)_4]$ (10 μmol), and 2 ml $AlOct_3$ (10 mM solution in toluene, 20 μmol) were added in glove box. The solution was kept stirring for 20 min at room temperature. Norbornene (2.5 ml, 2.65 M solution in toluene) and 1,3-butadiene(0.24 mL, 0.46 M solution in touene) were premixed and was added by a syringe. The polymerization was carried on for 1 h. The reaction was quenched by adding 0.5 mL isopropanol. The polymer was precipitated from acidified methanol and was dried under vacuum overnight.

B.2.5. References

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B.3. Block Copolymerization of Styrene and Butadiene

B.3.1. Introduction

The living polymerization of olefins has attracted much attention because of its usefulness for the synthesis of polymers with well-defined stereochemistry, controlled molecular weight, and narrow molecular weight distribution, terminal functions as well as block copolymers with defined block length and sequence.[1-6]

Styrene-butadiene block copolymers have received much attention because the stereoregularity of both blocks with respect to the commercially available Styrene-butadiene diblock copolymer and Styrene-butadiene-styrene triblock copolymer is expected to improve the mechanical and thermal properties. Zambelli and co-workers have reported that block copolymer consisting of *syn*-PS blocks and *cis*-PB blocks could be obtained with $CpTiX_3$ (Cp = C_5H_5, C_5Me_5; X = Cl, F, Me) activated with methylaluminoxane (MAO).[7-8] Syndiotactic polystyrene-*block*-*cis*-1,4-polybutadiene obtained via living polymerization has been reported by Shiono and co-workers.[9-10]

Okuda and co-workers have reported in 2004 that configurationally rigid bis(phenolato) group IV metal catalysts efficiently polymerize styrene with a high degree of stereo- and regiocontrol.[11-16] The specificity of the catalyst depends on a rigid ligand structure and a secondary insertion mode. Combining the stereoselectivity of the catalysts with (OSSO)-type ligands with enantioselectivity by asymmetric centers within the ligand framework gives a catalytic system that can produce homochiral isotactic polystyrenes.[17-18] Styrene and butadiene polymerization with the zirconium dibenzyl catalyst has a living nature. This catalyst made (isotactic polystyrene)-*block*-polybutadiene polymers accessible for the first time.[19]

B.3.2. Results and Discussion

B.3.2.1. Block Copolymerization of styrene and butadiene

According to previous studies, zirconium dibenzyl catalyst **1** shows living behaviour in styrene and butadiene homopolymerization as well as block copolymerization.[19] The living nature of this catalyst for styrene/butadiene block copolymerization was investigated by varying the chain length of polymers and the compositions. The block copolymer was prepared on condition that it has a high styrene content and high molecular weight. Polymers which have a high butadiene content and low molecular weight show two peaks in GPC analysis.

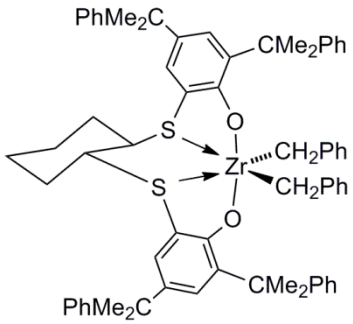

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Figure 1. Zirconium dibenzyl catalyst **1** for styrene/butadiene block copolymerization.

Table 1. Block copolymerization using **1**.

Run	[BD] / [styrene]	*T*	X_S : X_B	1,4-PBD (trans : cis)	1,4 : 1,2 PBD	M_n (g/mol)	M_w/ M_n	Peak
1	0.80	90 / 1	80 : 20	75 : 25	98 : 2	85,550	1.07	Single
2	1.12	90 / 1	53 : 47	70 : 30	98 : 2	115,580	1.06	Single
3	1.12	90 / 1	53 : 47	73 : 27	98 : 2	83,782	1.09	Single
4	1.12	90 / 1	66 : 34	77 : 23	98 : 2	59,037	1.06	Overlapped double
5	1.12	90 / 1	60 : 40	77 : 23	98 : 2	47,135	1.12	double

6	1.12	90 / 1	42 : 58	80 : 20	98 : 2	27,578	1.14	double
7	0.32	90 / 1	74 : 26	79 : 21	98 : 2	33,305	1.05	Single
8	3.36	25 / 3	86 : 14	76 : 24	98 : 2	16,949	1.04	Single
9	1.12	90 / 1	43 : 57	83 : 17	98 : 2	12,225	1.22	double
10	2.24	90 / 1	28 : 72	78 : 22	98 : 2	26,751	1.47	double
11	1.33	25 / 3	84 : 16	78 : 22	98 : 2	30,641	1.30	Single
12	1.24	50 / 3	81 : 19	81 : 19	98 : 2	36,582	1.23	Single
13	1.23	70 / 1	78 : 22	76 : 24	98 : 2	95,173	1.05	Single
14	1.12	90 / 1	57 : 43	78 : 22	98 : 2	153,450	1.24	Single

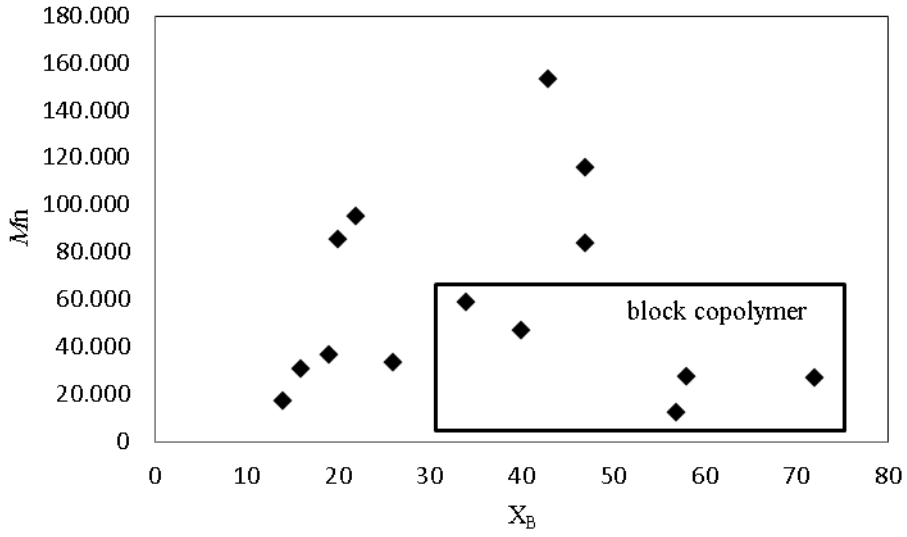


Figure 2. Region of block copolymer formation.

Butadiene/styrene block copolymers were prepared via reversed sequential addition because zirconium(IV) dibenzyl catalyst **1** displays living behaviour in butadiene and styrene polymerization. Butadiene is polymerized at 90 °C and cooled to room temperature before styrene was added. But styrene does not polymerize at room temperature and after raising

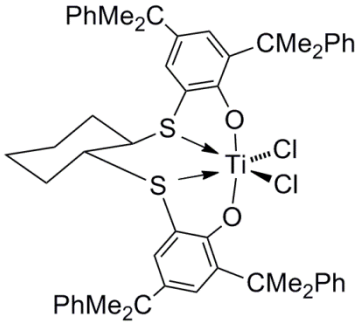
temperature to 90 °C, styrene was polymerized. The molecular distributions are slightly broader than those of styrene/butadiene block copolymers.

Table 2. Styrene/butadiene block copolymerization via reversed addition.

Run	Styrene (mmol)	[BD] / [styrene]	$X_S : X_B$	1,4-PBD (trans : cis)	M_n (g/mol)	M_w/M_n
1	4.36	0.25	83 : 17	80 : 20	79,494	1.29
2	1.40	0.32	79 : 21	83 : 17	42,504	1.14
3	5.76	0.70	60 : 40	77 : 23	108,360	1.42

Polymerization conditions: 1 μmol catalyst **1**, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$, t = 3 h, T = 90 °C.

It is known that aluminium alkyl induces chain transfer reactions during polymerization. Commercially available MAO solution contains trimethylaluminium which can hamper the living behavior of catalyst.[20-22] Thus, dried MAO was used with titanium dichloro catalyst **2** for block copolymerization. Block copolymer prepared by complex **2** with dried MAO has narrow molecular weight distributions. Butadiene is not copolymerized well at room temperature and conversion decreases as the butadiene feed ratio increases. Complex **2** activated dried MAO shows more *trans*-1,4 addition selectivity compared to zirconium(IV) dibenzyl complex **1** with $[(PhNMe_2H)(B(C_6F_5)_4]$.



2

Figure 3. Titanium dichloro complex **2** for styrene/butadiene block copolymerization.

Table 3. Styrene/butadiene block copolymerization using titanium dichloro catalyst **2** /MAO.

run	X_S (feed)	X_S (Copolymer)	Conversion (%)	M_n (PS)	M_w/M_n	M_n (PS-*b*-PB)	M_w/M_n	*trans* : *cis*	1,4 : 1,2
1	0.2	0.65	40	134,890	1.15	141,610	1.27	97 : 3	98 : 2
2	0.5	0.85	70	127,100	1.18	140,470	1.20	94 : 6	98 : 2
3	0.7	0.96	87	N.D.[1]	N.D.	155,840	1.36	N.D.	98 : 2

[1] N.D. = Not determined. Polymerization conditions: 1.3 mmol styrene, 1 µmol catalyst **2**, 1500 eq. dried MAO, t = 4 h, T = 25 °C.

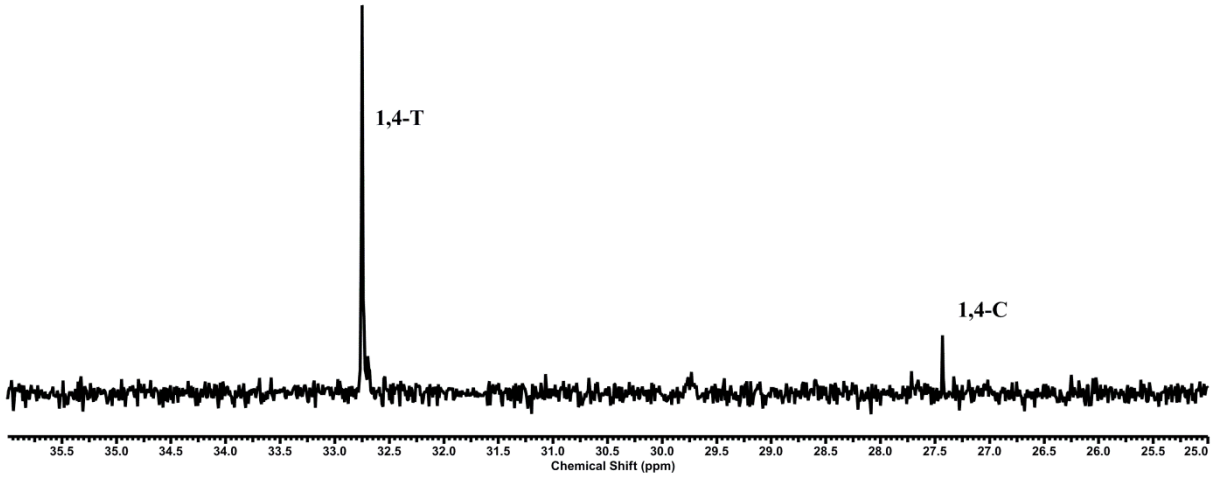


Figure 4. ^{13}C NMR spectrum of styrene/butadiene block copolymer in $CDCl_3$ at 25 °C.

B.3.2.2. Random Copolymerization of styrene and butadiene

Random copolymerization of styrene and butadiene is conducted to investigate the reactivity of styrene and butadiene monomer. Styrene and butadiene are copolymerized at room temperature and the conversion is less than 10%. ^{13}C NMR spectroscopy analysis shows that the styrene/butadiene copolymer contains no 1,2-addition product and a slightly enriched *trans*-1,4 vs *cis*-1,4 addition.[23] The reactivity ratios of $r_1 = k_{SS}/k_{SB}$ and $r_2 = k_{BB}/k_{BS}$ were determined using the Fineman-Ross method with the linear relationship:

$$[(1-F)/F]f = r_1 - r_2 f^2/F$$

where F and f are the butadiene/styrene molar ratios in the polymer (by ^{1}H NMR analysis) and the feed, respectively. The reactivity ratios obtained are r_1 = 1.3 and r_2 = 0.4. The r_2 value indicates a preference for insertion of styrene (vs. butadiene) if the last inserted monomer unit

in the growing polymer chain is butadiene. For $r_1r_2 < 1$, the copolymer tends to random distributions of its monomer unit.[23-25]

Table 4. Random copolymerization of styrene and butadiene.

Run	[BD] / [styrene]	$X_S : X_B$	Conversion of styrene (%)	Conversion of butadiene (%)	M_n (g/mol)	M_w/M_n
1	0	100 : 0	100	0	N.D.[1]	N.D.
2	0.1	94 : 6	81.3	54.5	69,265	1.45
3	0.36	79 : 21	24.0	17.7	32,132	1.42
4	1.0	63 : 37	9.7	5.7	22,523	1.41
5	1.5	54 : 46	8.3	4.7	22,590	1.35
6	2.0	46 : 54	5.7	3.3	27,425	1.34

1 N.D. = Not determined. Polymerization conditions: 10 µmol catalyst **1**, 1 eq. [$(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$, styrene 5.76 mmol, t = 3 h, T = 25 °C.

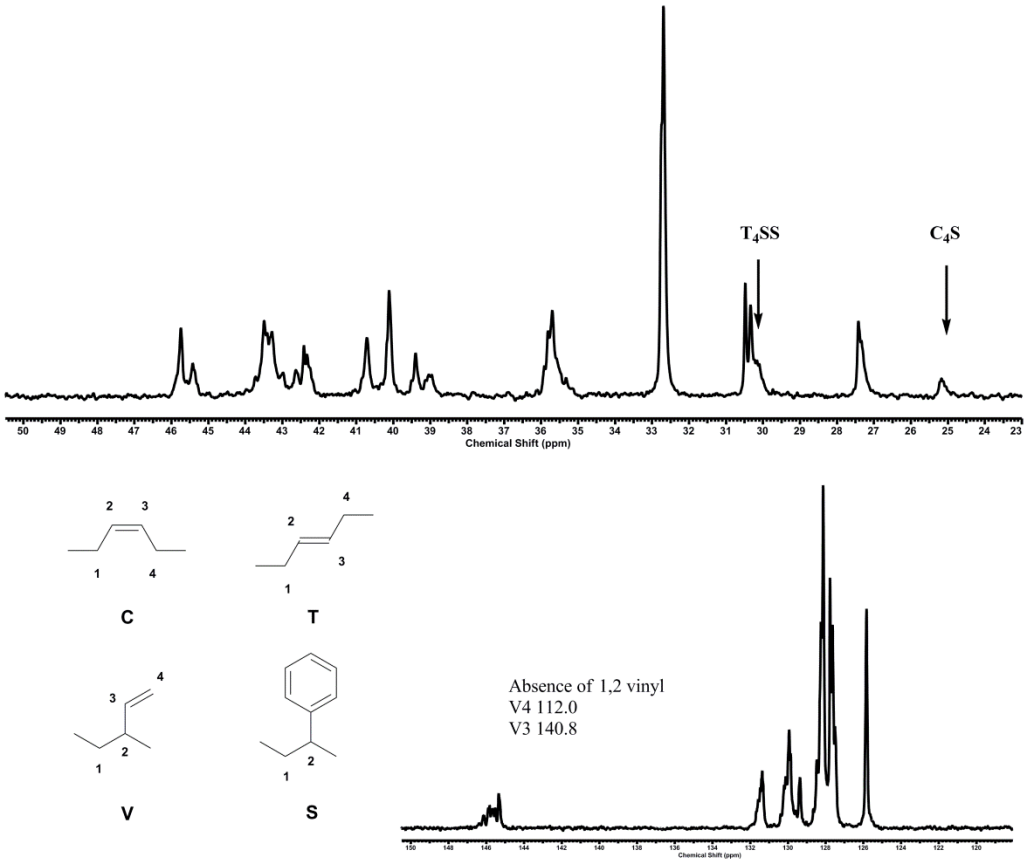
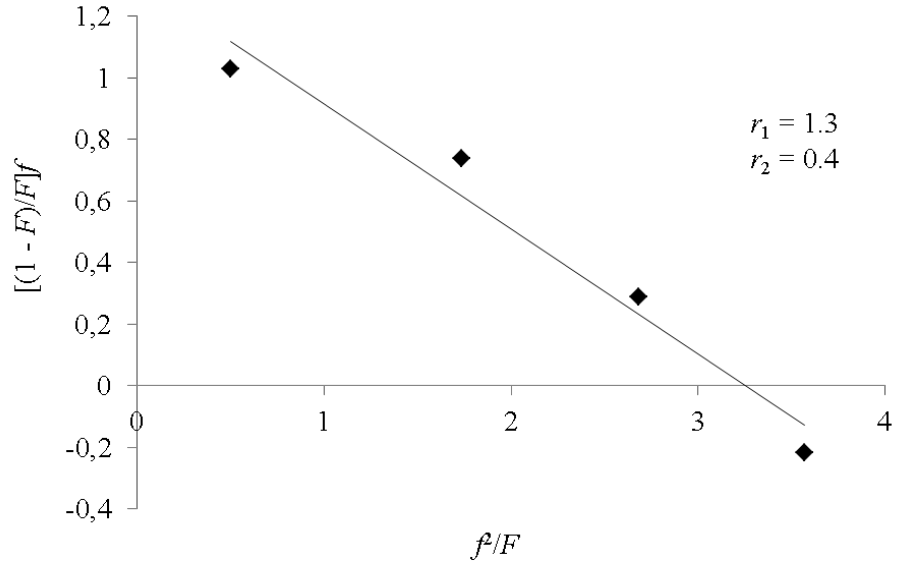


Figure 5. ^{13}C NMR spectrum of styrene/butadiene random copolymer in $CDCl_3$ at 25 °C.



$[(1 - F)/F]f = r_1 - r_2 f^2/F$

F : butadiene/styrene molar ratios in the polymer

f : butadiene/styrene molar ratios in the feed

r_1 : k_{SS}/k_{SB}

r_2 : k_{BB}/k_{BS}

Figure 6. Fineman-Ross plot of styrene/butadiene random copolymer.

B.3.2.3. Preparation of styrene/ethylene copolymer

Butadiene/styrene copolymer is hydrogenated using Wilkinson catalyst and transformed to budtadiene/ethylene copolymer.[26-29] Whereas $RuCl_2(PPh_3)_3$ catalyzed the hydrogenation reaction without formation of a side product, a partially dimerized polymer was detected in GPC analysis using $RhCl(PPh_3)_3$. The Ethylene/styrene copolymer is not soluble in chloroform and only polystyrene peaks are observed in ^1H and ^{13}C NMR spectra. Polyethylene peaks are obtained at 100°C in dichlorobenzene-d_4.

The number average molecular weight decreases due to the difference in hydrodynamic volume and the molecular weight distributions are still narrow. ^1H and ^{13}C NMR spectra show the disappearance of polybutadiene peaks and the appearance of polyethylene peaks in the polystyrene/polyethylene block copolymer spectrum.

Table 5. Hydrogenation of styrene/butadiene copolymer.

Run	iPS-*b*-PBD			Hydrogenation			iPS-*b*-PE	
1	X_S : X_B	M_n (g/mol)	M_w/ M_n	Catalyst	*t* (h)	Pressure (bar)	M_n (g/mol)	M_w/M_n
2	64 : 36	124,680	1.09	$RuCl_2(PPh_3)_3$	38	30	106,760	1.03
3	53 : 47	115,580	1.06	$RuCl_2(PPh_3)_3$	64	50	106,470	1.03
4	80 : 20	85,550	1.07	$RhCl(PPh_3)_3$	24	50	90,108 (188,280)	1.04 (1.05)

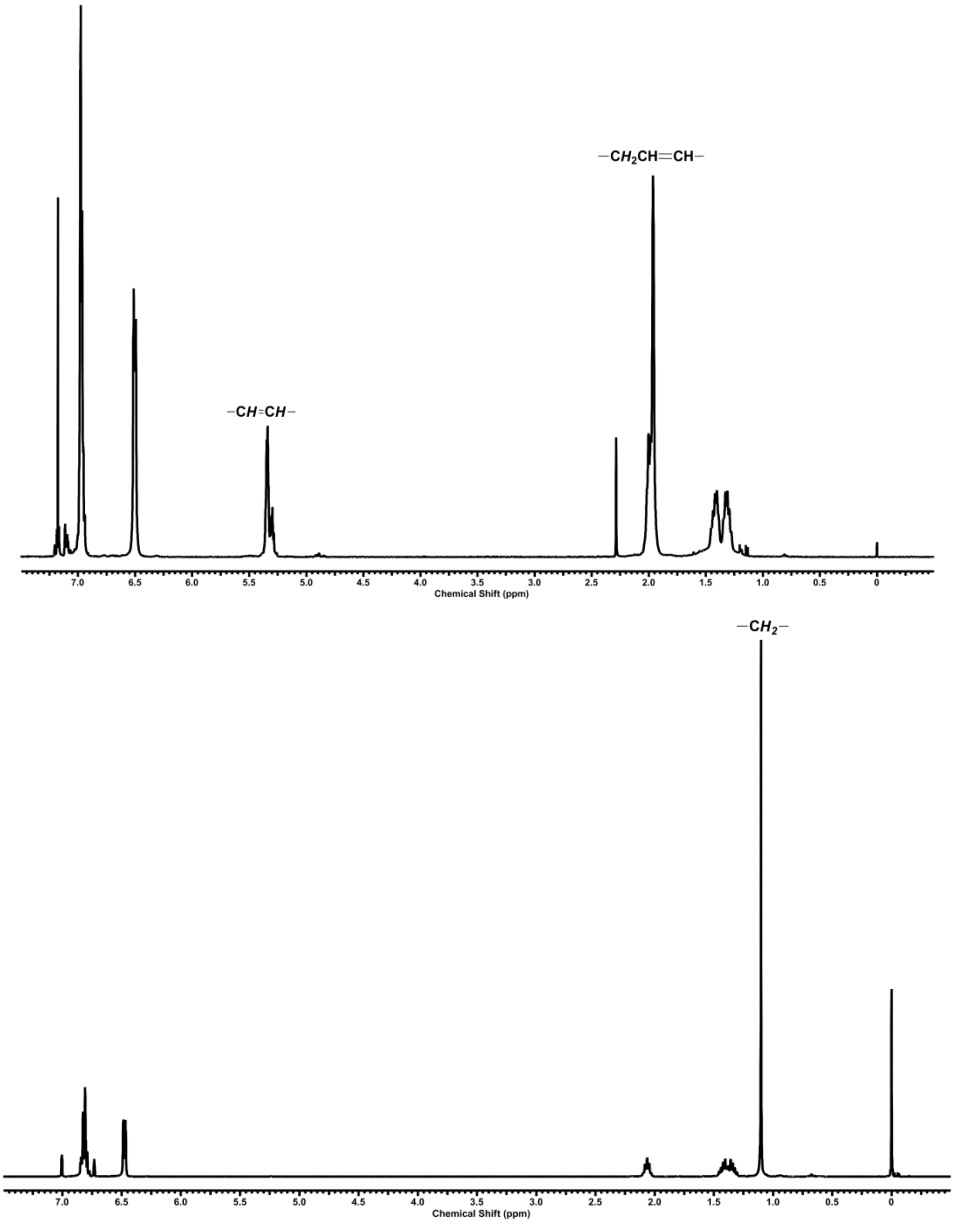


Figure 7. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of styrene/butadiene block copolymer (above) and ^{1}H NMR spectrum ($C_6D_4Cl_2$, 100 °C) of styrene/ethylene block copolymer (below).

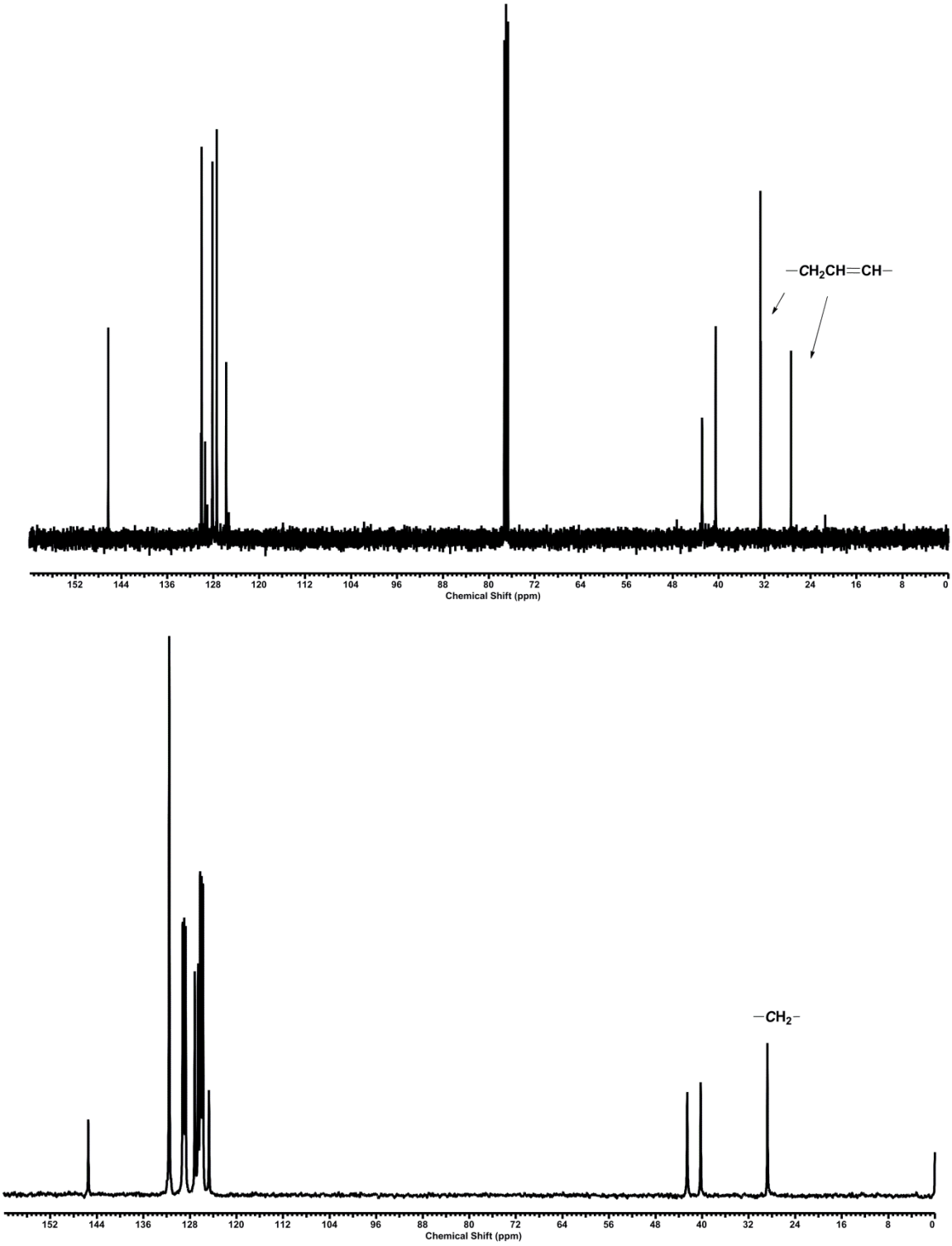


Figure 8. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of styrene/butadiene block copolymer (above) and ^{13}C NMR spectrum ($C_6D_4Cl_2$, 100 °C) of styrene/ethylene block copolymer (below).

The thermal behavior of ethylene/styrene block copolymer was investigated. To determine the thermal behavior, melting transitions were analyzed by Differential Scanning Calorimetry (DSC). A standard DSC measurement consists of two heating and cooling cycles. Since

isotactic polystyrene is a slowly crystallizing polymer, it shows a weak melting transition in the second heating curve.[30-36] However, rapidly crystallizing polyethylene may lead to a faster crystallization of the polystyrene in block copolymer. For a 36 mol % butadiene containing block copolymer, the second melting transition is not found. The hydrogenated styrene/ethylene block copolymer shows a weak second melting transition. Block copolymer containing 47 mol % butadiene was hydrogenated and its second melting transition is clearly seen. Thus rapid crystallization of isotactic polystyrene is induced by rapid crystallization of polyethylene.

Table 6. Crystallization of isotactic polystyrene induced by polyethylene.

Run	$X_S : X_B$	M_n	M_w/M_n	1st Heating		2nd Heating	
				T_m (°C)	Δ H (J/g)	T_m (°C)	Δ H (J/g)
1	64 : 36	124,680	1.09	222.9	19.27	Not found	
2	-	106,760	1.03	221.7	17.93	223.8	3.38
3	53 : 47	115,580	1.06	224.2	17.50	224.4	0.66
4	-	106,470	1.03	224.3	13.22	224.9	8.27

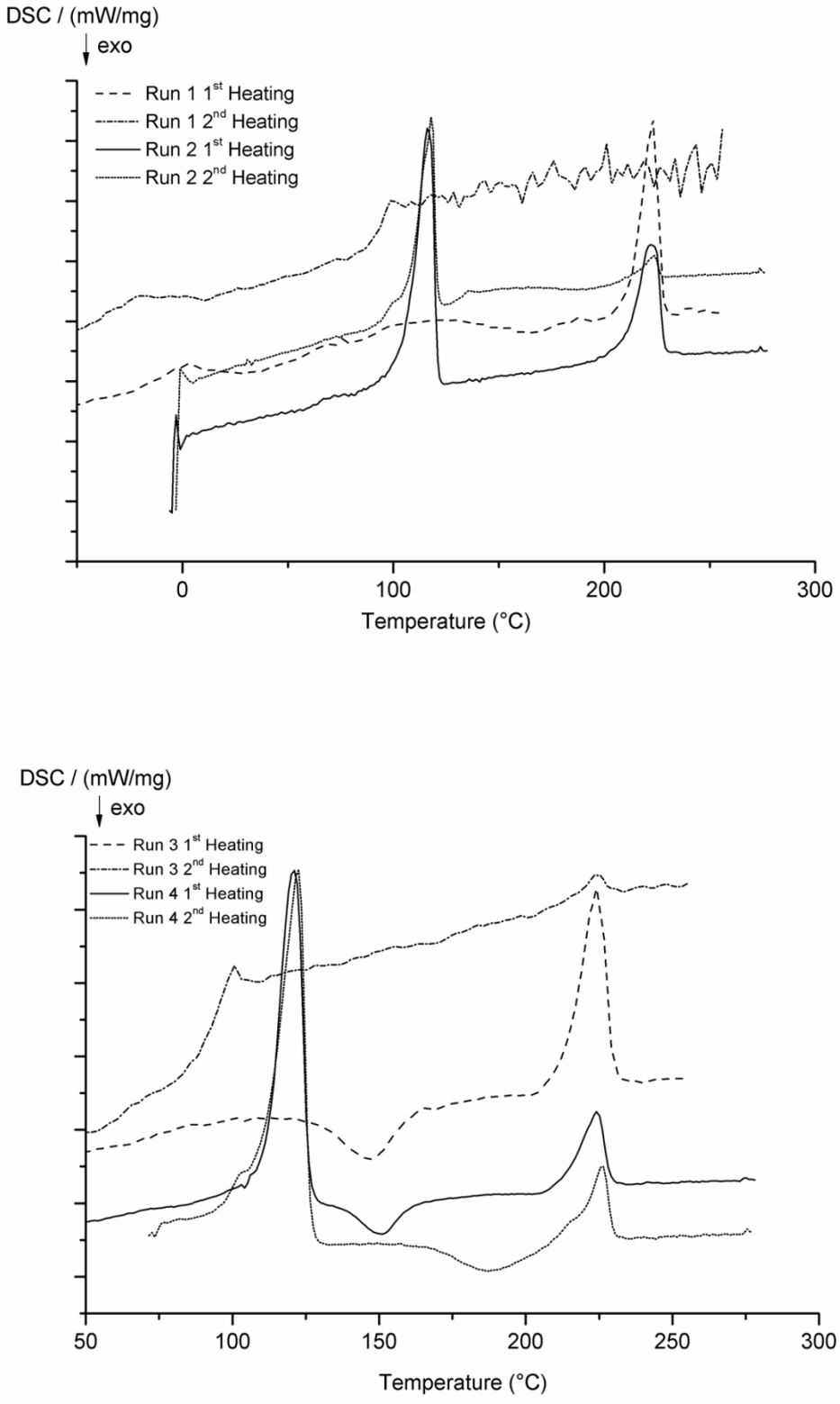


Figure 9. Thermal behaviour of styrene/butadiene (above) and styrene/ethylene block copolymer (below).

B.3.2.4. Oligomerization of butadiene

Oligomerization of butadiene is conducted using 1-hexene as a chain transfer agent. Due to impurities in 1-hexene, the 1-hexene/butadiene ratio can not exceed 2.41 and conversion becones low at that 1-hexene content. After adding 10 eq. of trisoctylaluminium, oligobutadienes are obtained without significant loss of activity. Oligo(1-hexene) is also obtained during oligomerization of butadiene and is separated by silica column with hexanes. Oligomerization of 1-hexene is not regioselective since similar amounts of 1,2- and 2,1-insertion products form (Figure 11).[37]

Table 7. Oligomerization of butadiene with 2 eq. of trioctylaluminium.

Run	1-Hexene (ml)	1-Hexene / Butadiene	M_n	M_w/M_n
1	0,00	0,00	66357	1,10
2	0,25	0,40	53462	1,21
3	0,50	0,69	24388	1,48
4	1,00	1,61	10676	1,49
5	1,50	2,41	8748	1,50

Polymerization conditions : 10 µmol catalyst **1**, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$, 1,3-butadiene, 1-hexene premixed and added, t = 2 h, T = 90 °C.

Table 8. Oligomerization of butadiene with 20 eq. of trioctylaluminium.

Run	1-Hexene (ml)	1-Hexene / Butadiene	M_n	M_w/M_n
1	0,00	0,00	66357	1,10
2	0,10	0,16	33619	1,85
3	0,50	0,80	19400	2,04
4	1,00	1,61	8982	1,62
5	2,00	3,21	3418	1,77
6	3,00	4,82	1561	1,91

Polymerization conditions : 10 µmol catalyst **1**, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 20 eq. $Al(^nOct)_3$, 1,3-butadiene, 1-hexene premixed and added, t = 2 h, T = 90 °C.

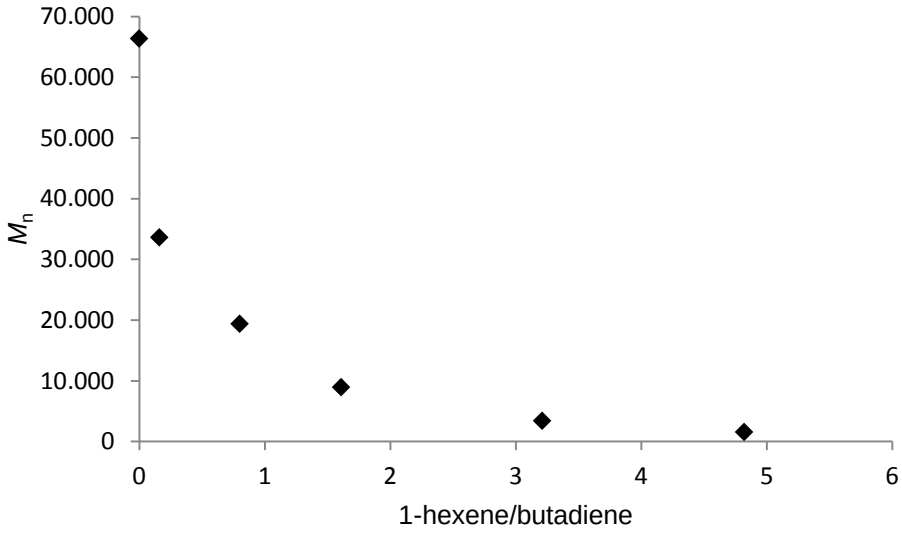


Figure 10. Dependence of the number-average molecular weight (M_n) on the 1-hexene/butadiene ratio.

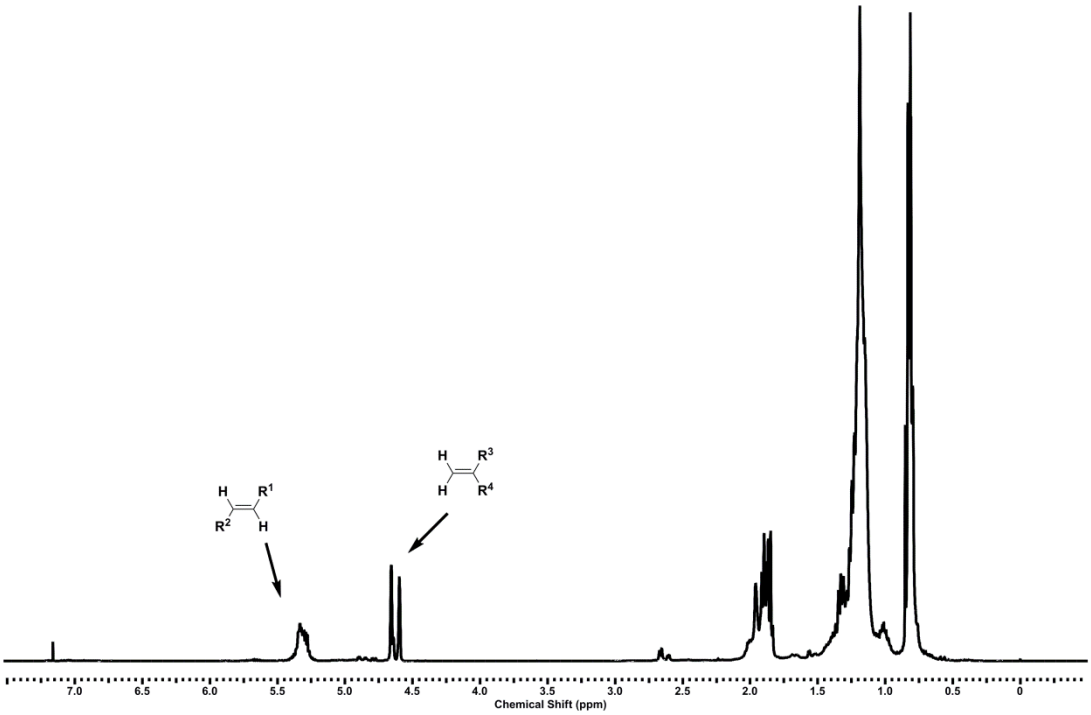


Figure 11. ^{1}H NMR spectrum of 1,2- and 2,1-insertion products of oligo(1-hexene) in $CDCl_3$ at 25 °C.

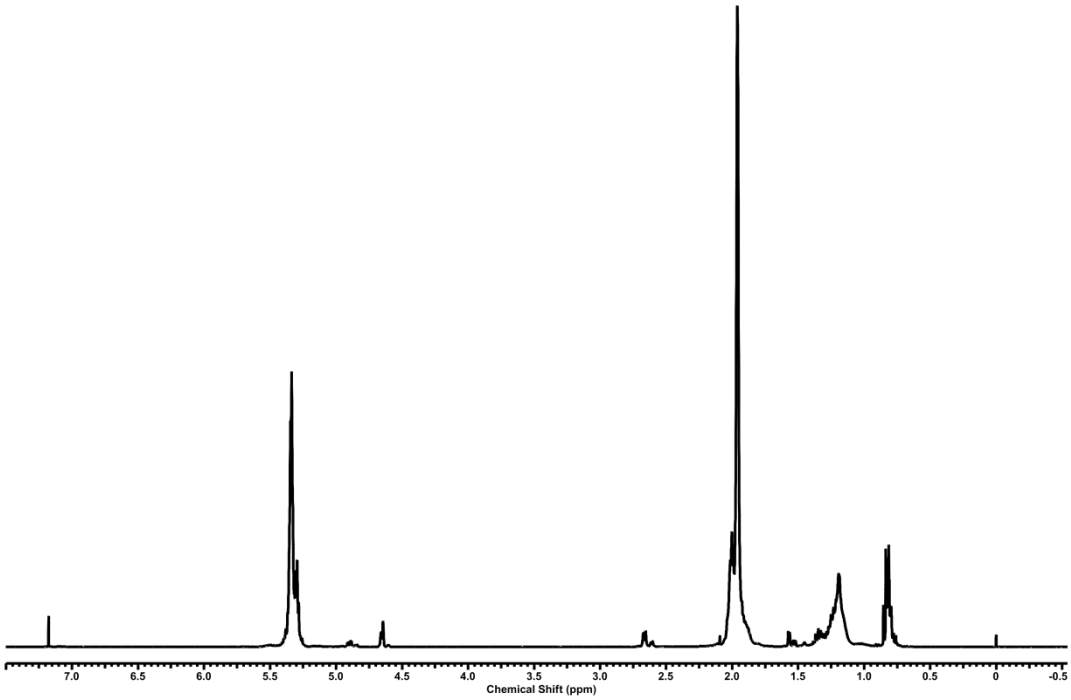
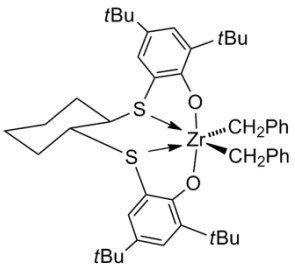


Figure 12. ^{1}H NMR spectrum of oligo(1-hexene) terminated oligo(butadiene) in $CDCl_3$ at 25 °C.

B.3.2.5. Homopolymerization of isoprene

Isoprene is polymerized using the zirconium dibenzyl complex **3**. The corresponding cumyl substituted complex **1** is inactive for isoprene polymerization due to the bulky nature of isoprene monomer. The di-*tert*-butyl substituted complex **3** is active at 90 °C but the conversion is less than 20% even at extended reaction time. Polysisoprene has a high content of 1,4-addition product and there is no high selectivity between *trans*- and *cis*-1,4 addition. The 1,2 and 1,4-addition ratio is calculated by the relative peak area of vinyl protons in the ^{1}H NMR spectrum and the *trans*- and *cis*-3,4 addition ratio is calculated by the relative peak area of the methyl peak in the ^{13}C NMR spectrum.[38-39]



rac-[Zr] catalyst **3**

Figure 13. Zirconium dibenzyl catalyst **3** for isoprene polymerization.

Table 9. Polymerization of isoprene using catalyst **3**.

run	cat	*T* / *t* (°C / h)	conversion (%)	*trans*-1,4 : *cis*-1,4 (%)	Vinyl-1,4 : 3,4 (%)	M_n	M_w/M_n
1	**1**	90 / 3	<< 1%	N.D.[1]	84:16	N.D.	N.D.
2	**3**	70 / 6	6.6	76:24	96:4	N.D.	N.D.
3	**3**	90 / 3	10.4	53:47	94:6	27,493	1.2
4	**3**	90 / 6	15.4	56:44	94:6	30,265	2.2

[1] N.D. = Not determined. Polymerization conditions : 10 µmol catalyst **3**, 1 eq. $[(PhNMe_2H)(B(C_6F_5)_4]$, 2 eq. $Al(^nOct)_3$, toluene 9 ml, isoprene, 2mL (20 mmol).

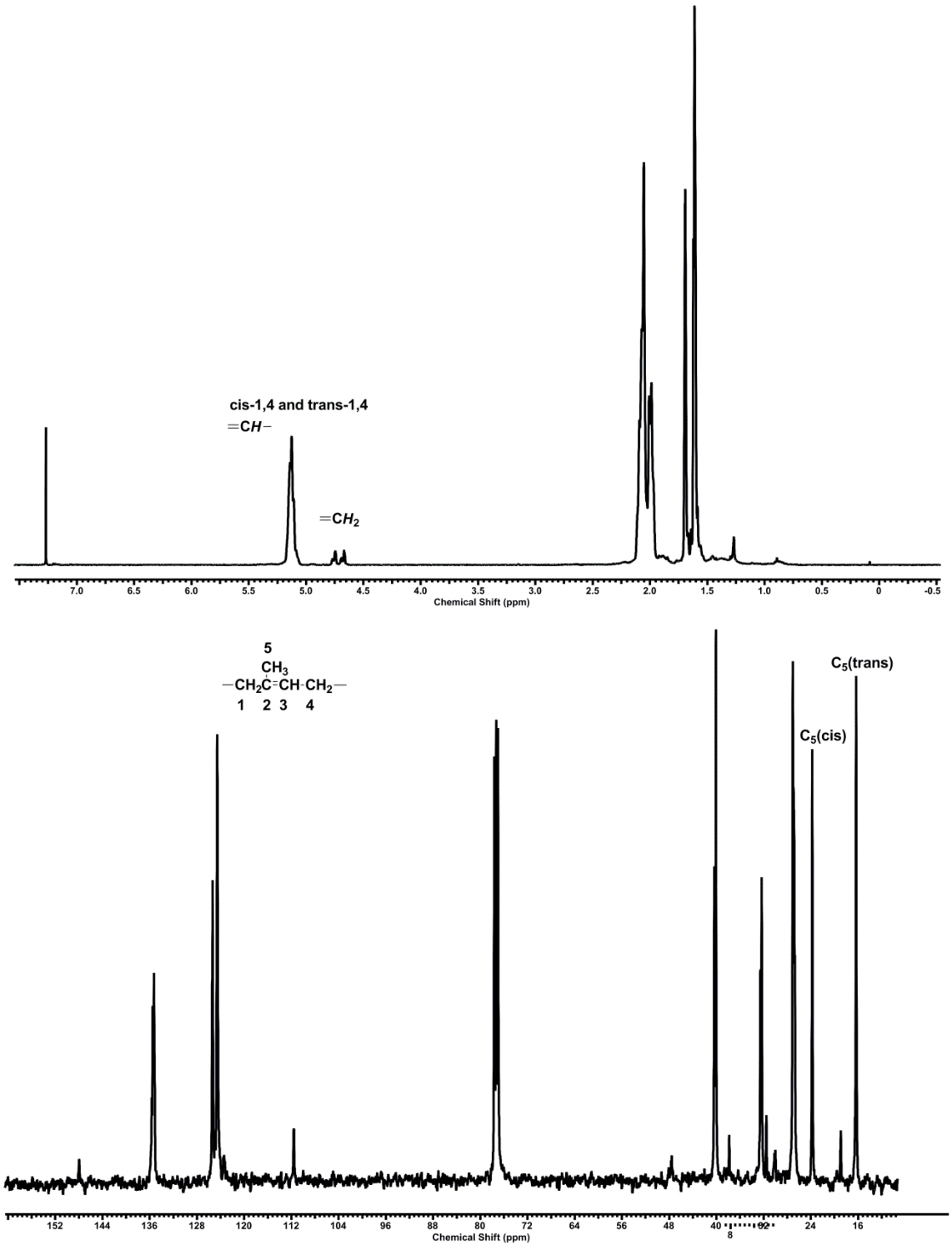
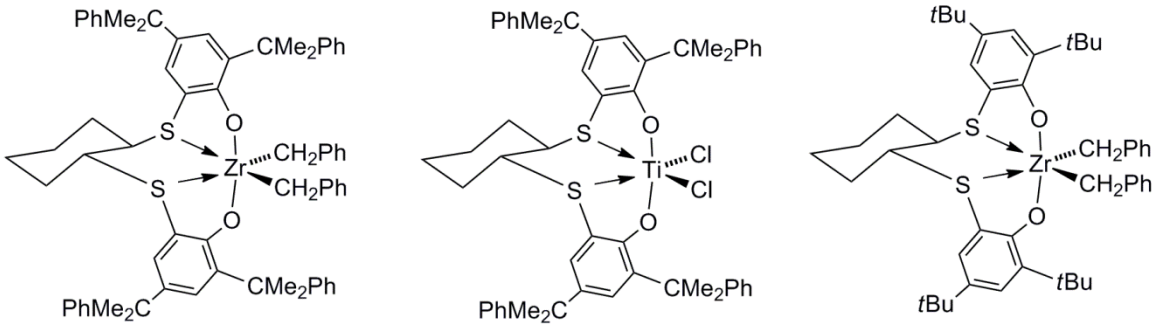


Figure 14. ^{1}H NMR (above) and ^{13}C NMR (below) spectrum of polyisoprene using *rac*-[Zr] catalyst **3** in $CDCl_3$ at 25 °C.

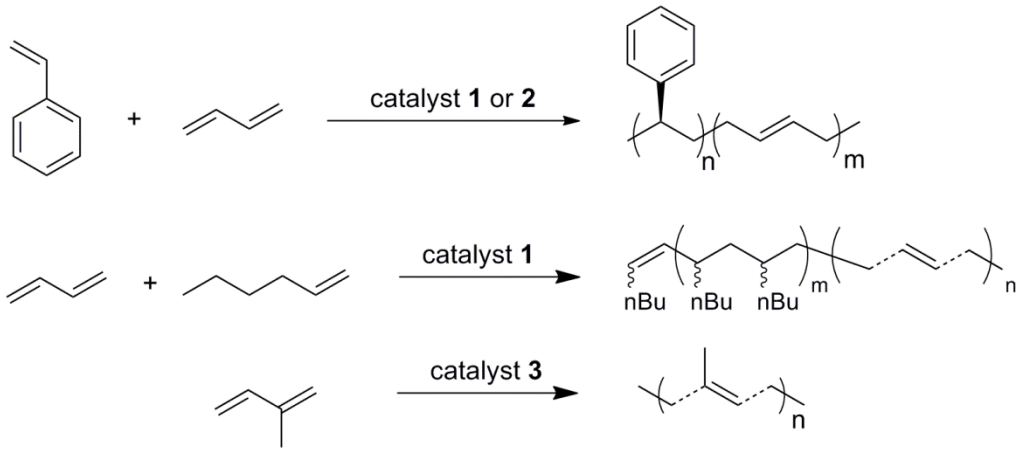
B.1.3. Concluding Remarks

Styrene/butadiene block copolymer was obtained using zirconium dibenzyl catalyst **1** under conditions that lead to high styrene content and high molecular weight. Due to the living nature of catalyst in butadiene polymerization, reversed sequential addition of monomer is also possible. Titanium(IV) complex **2** with dried MAO shows more *trans*-1,4 addition selectivity compared to zirconium dibenzyl complex **1** with $[(PhNMe_2HPh)(B(C_6F_5)_4]$.

To investigate reactivities of monomers, random copolymerization was conducted. Styrene/ethylene block copolymer was prepared via hydrogenation of styrene/butadiene block copolymer. Styrene/ethylene copolymer shows a melting transition in the second heating in DSC analysis due to induced crystallization by polyethylene chain. Butadiene oligomer was obtained using 1-hexene as a chain transfer agent. In this process, oligo(1-hexene)s are also generated. Polyisoprene was prepared with low conversion using **3**.



1 **2** **3**



B.1.4. Experimental Section

Synthesis of rac-dibenzyl-(dithiacyclohexanediyl-2,2'-bis(4,6-di-cumylphenolato))-zirconium

To a solution consisting of $Zr(Bn)_4$ (0.48 mmol) in toluene (15 mL), the ligand (0.48 mmol) in toluene (20 mL) was slowly added at -60 °C. The solution was allowed to warm to room temperature and stirred for further two hours. After evaporating the solvents under vacuum pentane was added and the product was obtained as a yellow powder. (0.35 mmol, 73 %); ^{1}H NMR (C_6D_6): δ 0.55(m, 2 H, cyclohexyl), 1.08(m, 2 H, cyclohexyl), 1.12(d, $^2J_{HH}$ = 8.53 Hz, 2 H, ZrC*H*$_2$Ph), 1.24 (m, 2 H, cyclohexyl), 1.58(s, 6 H, C(C*H*$_3$)$_2$(C_6H_5)), 1.61 (s, 6 H, C(C*H*$_3$)$_2$(C_6H^5)), 1.65 (s, 6 H, C(C*H*$_3$)$_2$(C_6H_5)), 1.66 (s, 6 H, C(C*H*$_3$)$_2$(C_6H_5)), 1.71 (m, 2 H, cyclohexyl), 1.87(d, $^2J_{HH}$ = 8.53 Hz, 2 H, ZrC*H*$_2$Ph), 1.91 (m, 2 H, SC*H*), 6.41 (d, $^4J_{HH}$ = 7.28 Hz, 4 H, Zr-CH_2-C_6H_5-2-*H*), 6.82 (d, $^4J_{HH}$ = 2.01 Hy, 2 H, C6H2-3-*H*), 7.20-6.86 (m, 26 H, C(CH3)2(C6*H*5) and ZrCH_2C_6*H*$_5$), 7.50(d, $^4J_{HH}$ = 2.01 Hz, 2 H, C_6H_2-5-*H*) ppm

Typical procedure for the synthesis of block copolymers.

Into a 20 mL flask equipped with a magnetic stirrer, toluene (7 mL), the catalyst (10 μmol), [PhNMe_2H][B(C_6F_5)$_4$] (10 μmol), and 2 ml of $AlOct_3$ (20 μmol) were added. The solution was kept stirring for 20 min at room temperature. The appropriate amount of styrene was added via syringe and the mixture was stirred for 30 min at room temperature. Then the appropriate amount of 1,3-butadiene was added and the reaction solution was heated at 90 °C. After the appropriate reaction time, the reaction was quenched through the addition of 0.5 mL of isopropanol. The polymer was precipitated into acidified methanol (3 % HCl, 100 mL) and dried under vacuum overnight.

Typical procedure for the synthesis of block copolymers.

Into a 20 mL flask equipped with a magnetic stirrer, toluene (7 mL), the catalyst (10 μmol), [PhNMe_2H][B(C_6F_5)$_4$] (10 μmol), and 2 ml of $AlOct_3$ (20 μmol) were added. The solution was kept stirring for 20 min at room temperature. The appropriate amount of styrene was added by a syringe and the mixture was stirred for 2 h at room temperature. Then the appropriate amount of 1,3-butadiene was added and the reaction solution was stirred for 2 h at room temperature. After the appropriate reaction time, the reaction was quenched by the

addition of 0.5 mL of isopropanol. The polymer was precipitated from acidified methanol (3 % HCl, 100 mL) and dried under vacuum overnight.

Typical procedure for the synthesis of random copolymers.

Into a 20 mL flask equipped with a magnetic stirrer, toluene (9 mL), the catalyst (1.0 μmol), and dried MAO (70 mg) were added. The appropriate amount of styrene and butadiene were premixed and added via syringe and the mixture was stirred for 3 h at room temperature. The reaction was quenched by the addition of 0.5 mL of isopropanol. The polymer was precipitated from acidified methanol (3 % HCl, 100 mL) and dried under vacuum overnight.

Typical procedure for the hydrogenation of styrene/butadiene block copolymer.

Into a 500 mL autoclave with a magnetic stirrer, toluene (50 mL), $RuCl_2(PPh_3)_3$ (40 mg), Triphenylphosphine (10 mg), and styrene/butadiene block copolymer (0.5 g) were added. The reactor was pressurized with hydrogen to 30 bar and the temperauture was raised to 100 °C. The solution was kept stirring for 38 h at room temperature. The reaction was quenched by the addition of 0.5 mL of isopropanol. The polymer was precipitated from acidified methanol (3 % HCl, 100 mL) and dried under vacuum overnight.

Typical procedure for the oligomerization of butadiene.

Into a 20 mL flask equipped with a magnetic stirrer, toluene (7 mL), the catalyst (10 μmol), $[PhNMe_2H][B(C_6F_5)_4]$ (10 μmol), and 2 ml of $AlOct_3$ (20 μmol) were added. The solution was kept stirring for 20 min at room temperature. The appropriate amount of butadiene and 1-hexene as well as $AlOct_3$ (180 μmol) were premixed and added via syringe and the mixture was stirred for 2 h at 90 °C. The reaction was quenched by the addition of 0.5 mL of isopropanol. The polymer was precipitated from acidified methanol (3 % HCl, 100 mL) and dried under vacuum overnight.

Typical procedure for the homopolymerization of isoprene.

Into a 20 mL flask equipped with a magnetic stirrer, toluene (7 mL), the catalyst (10 μmol), $[PhNMe_2H][B(C_6F_5)_4]$ (10 μmol), and 2 ml of $AlOct_3$ (20 μmol) were added. The solution was kept stirring for 20 min at room temperature. Isoprene (2 mL, 20 mmol) was added by a syringe and the mixture was stirred for 2 h at 90 °C. The reaction was quenched by the

addition of 0.5 mL of isopropanol. The polymer was precipitated from acidified methanol (3 % HCl, 100 mL) and dried under vacuum overnight.

B.1.5. References

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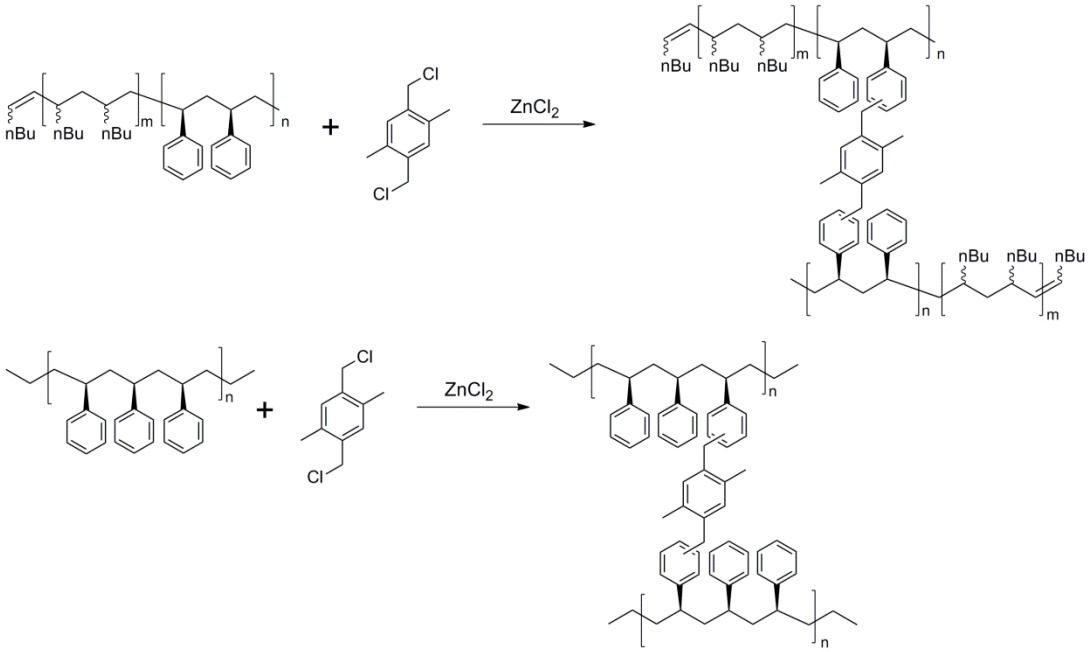
C. Summary

The main objective of this thesis is the synthesis of optically active polyolefins. The second is to develop styrene/butadiene block and styrene/ethylene block copolymers using the living polymerization with zirconium catalyst containing an (OSSO)-type bis(phenolate) ligand.

Chapter 1 describes the development of optically active crosslinked homochiral polystyrene and oligostyrenes. Homochiral polystyrenes are crosslinked to induce helical structure in solution and the chiral recognition ability was investigated. Optically active oligostyrenes are crosslinked and relations between optical activity and the degree of crosslinking are described.

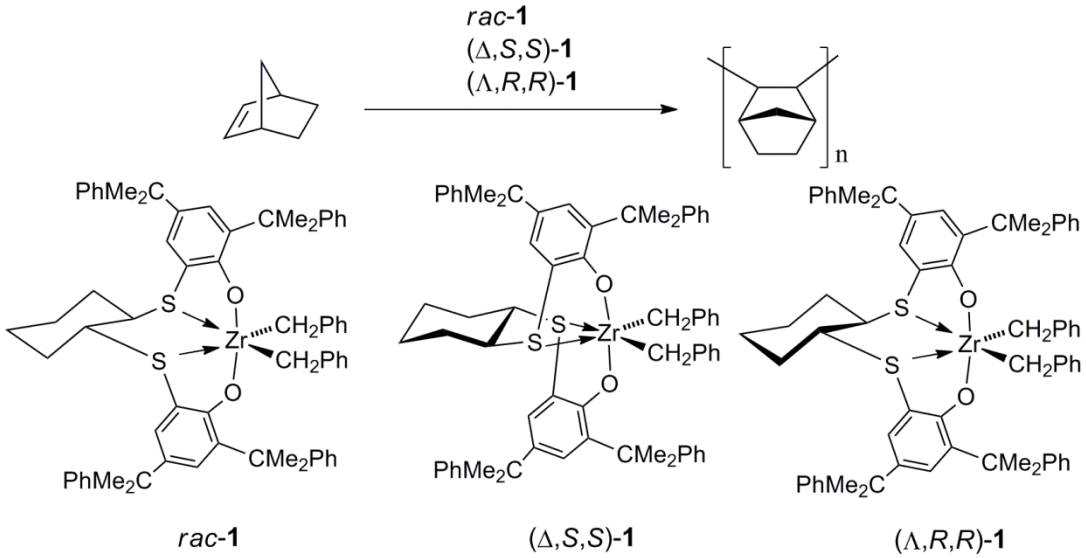


Scheme 1. Crosslinking of optically active polystyrene and oligostyrene using 1,4-dimethyl-2,5-di(chloromethyl)benzene as a crosslinker.

Chiral isotactic polystyrene was crosslinked in solution or suspension using 1,4-bis(chloromethyl)-2,5-dimethylbenzene to form a microgel. Chiral isotactic crosslinked polystyrene can be used as material for column chromatography due to its pores produced by crosslinking. Chiral crosslinked oligostyrenes were synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy. Crosslinked chiral oligostyrenes are optically active and their specific rotations vary depending on the degree of crosslinking. The size of crosslinked chiral oligostyrene is analyzed by light scattering method. The chiral recognition ability of

crosslinked chiral oligostyrene was investigated by selective absorption, but oligostyrenes do not show chiral recognition ability.

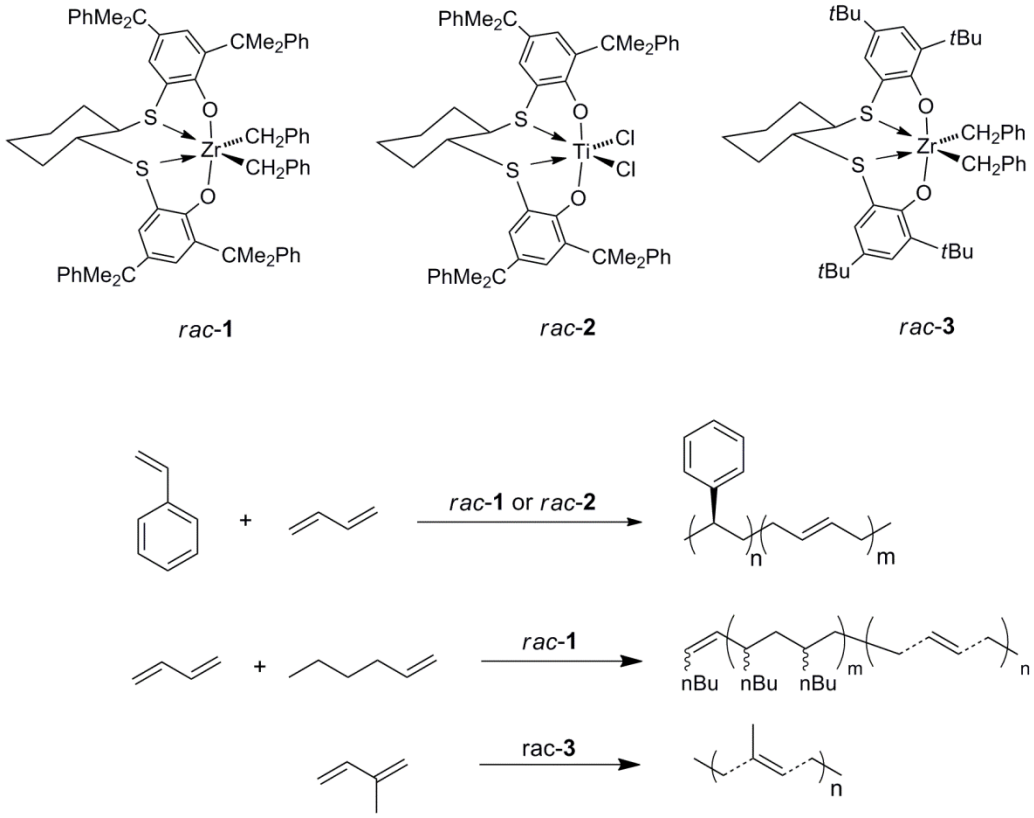
In chapter 2, the synthesis of optically active polynorbornenes is described. The polymerization results of norbornene and optical activities of polynorbornene are reported. Results of hydrooligomerization and deuteriooligomerization to investigate the tacticity as well as the structure of polynorbornene are described.



Scheme 2. Polymerization of norbornene using zirconium catalyst.

Polynorbornene was produced using racemic and enantiopure zirconium complexes with (OSSO)-type ligands. Polynorbornenes are addition polymers in nature and have narrow molecular weight distributions. To determine their tacticity, hydrooligomerization was performed. The C_2 symmetric nature of the zirconium complex is responsible for the diisotactic insertion. The termination position of deuteriooligomerization suggests that polynorbornene produced by *rac*-**1** has no C7 linkage. Optically active Polynorbornene was produced using enantiopure zirconium catalyst (Δ,*S*,*S*)-**1** and (Λ,*R*,*R*)-**1**, suggesting that the optical activity of polynorbornene comes from helices with a fixed sense of rotation.

Chapter 3 describes block copolymerization of styrene and butadiene using *rac*-**1** and *rac*-**2** catalysts. Preparation of a styrene/ethylene block copolymer via hydrogenation of styrene/butadiene block copolymer is described. Preparation of a butadiene oligomer using 1-hexene as a chain transfer agent is reported. Polyisoprene was prepared using *rac*-**3** catalyst which has *tert*-butyl substituents on the phenyl ring of the ligand.



Scheme 3. Polymerization of styrene, butadiene and isoprene.

A styrene/butadiene block copolymer was prepared using *rac*-**1** on conditions that give high styrene content and high molecular weight. Due to the living nature of the butadiene polymerization, reversed sequential addition of monomer is also possible. Titanium complex *rac*-**2** activated dried MAO shows more *trans*-1,4 addition selectivity compared to zirconium complex *rac*-**1** with [($PhNMe_2H$)($B(C_6F_5)_4$]. To investigate reactivities of monomers, random copolymerization was conducted. Styrene/ethylene block copolymer was prepared via hydrogenation of styrene/butadiene block copolymer. Styrene/ethylene copolymer shows a melting transition in the second heating in DSC analysis due to induced crystallization by polyethylene chain. Butadiene oligomer was made using 1-hexene as a chain transfer agent. Polyisoprene was prepared using *rac*-**3** which has tert-butyl substituents with low conversion.

D. Appendix

D.1. Experimental Details

All air sensitive operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques.

Diethyl ether, THF, and toluene were dried over sodium benzophenone ketyl. CH_2Cl_2 was dried over CaH_2. All solvents were distilled prior to use. Alternatively, THF, Et_2O, pentane, toluene, and CH_2Cl_2 were dried using an MBraun SPS-800 solvent purification system.

NMR spectra were recorded on Bruker Avance II 400 MHz at 25 °C (1H: 400 MHz; 13C{1H}: 100.1 MHz). Chemical shifts for ^{1}H and ^{13}C NMR spectra are referenced internally using the residual solvent resonances. Elemental analyses were performed by the Microanalytical Laboratory of the department of organic chemistry. Molecular weights of oligomers and polymers were measured using Agilent 1100 series gel permeation chromatography (GPC) at 30 °C in THF and calibrated with respect to polystyrene standards. Specific optical rotation measurements were performed using a Perkin Elmer 241 Digital Polarimeter or a Jasco P-2000 Digital polarimeter (path length 10 cm, volume 1 mL, λ = 589.3 nm at 23°C).

D.2. X-Ray Structure Analysis

The crystallographic data were collected by Prof. Dr. Ulli Englert and coworkers using Mo-Kα radiation on a Bruker AXS diffractometer with a CCD area detector using ω scans. The SMART program package was used to determine the unit-cell parameters and for data collection; the raw frame data were processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXS-97 programs. The crystal structure was solved by Dr. Thomas P. Spaniol.

Table 1. Crystallographic data and refinement parameters meso,meso,meso norbornene tetramer.

X-ray	
Crystal size (mm^3)	0.30 × 0.17 × 0.11
Empirical fomula	$C_{28}H_{42}$
M_r (g $mol^{-1)}$	378.62
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.5398(9)
b (Å)	11.4540(11)
c (Å)	19.6650(18)
α (°)	90
β (°)	90.517(2)
γ (°)	90
V ($Å^3$)	2148.7(3)
Z	4
D_{calc} (g cm^{-3})	1.170
T (K)	100(2)
μ(Mo Kα) (mm^{-1})	0.065
Wavelength (Å)	0.71073
F(000)	840.0
θ Range (°)	2.73-24.19
Index ranges	-11≤h≤11, -14≤k≤14, -24≤l≤24
Number of reflections collected	25110
Number of independent reflections (R_{int})	4389 (0.1392)
Data/restraints/parameters	4389 / 0 / 253
Goodness-of-fit on F^2	1.042
R_1, wR_2 [I> 2σ (I)]	0.0769, 0.1947
R_1, wR_2 (all data)	0.1217, 0.2195
Refinement method	Full-matrix least squares on F^2
Largest difference peak and hole (e $Å^{-3}$)	0.807 and -0.300
Method of structure solution	SIR-92 (Altomare 1992)
Method of refinement	SHELXL-97 (Sheldrick, 1997)

D.3. Curriculum Vitae

Biographical

Date of birth, place of birth	11.12.1975, Seoul.

Education

Postgraduate Studies

08/2008 - present	Doctoral Thesis under the supervision of Prof. Dr. Jun Okuda (RWTH Aachen University) *Chiral and Optically Active Polymers from Hydrocarbon Monomers*.

Undergraduate Studies

03/1998 - 02/2000	Master Thesis under the supervision of Prof. Dr. Young Gyu Kim (Seoul National University) *Synthesis of C7- and C12- Phytosphingosine Analogs and Assignment Study of the Relative Stereochemistry*.
03/1994 - 02/1998	Undergraduate studies in chemistry and chemical engineering (Seoul National University)

Secondary Education

03/1991 - 02/1994	Yusin High School, Suwon, Korea
03/1988 - 02/1991	Imok Middle School, Suwon, Korea
03/1982 - 02/1988	Ingae Elementary School, Suwon, Korea

Professional and Research Experience

06/2003 - 07/2008	Researcher (PEP Team, Polyolefin Research & Development Center, LG Chem, Daejeon, Korea) *Development of new metallocene catalyst for polyolefin elastomers*
03/2000 - 05/2003	Researcher (Department of Catalyst & Process Team, Research Center, Samsung General Chemicals, Daejeon, Korea) *Development of new catalyst for LLDPE*

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J. Jeon, M. Shin, J. W. You, J. S. Oh, J. G. Bae, S. H. Jung and Y. G. Kim, "Highly *anti*-Selective Dihydroxylation of 1,2-Dialkyl Substituted (*Z*)-Allylic Amines: Stereoselective Synthesis of a $_D$-*ribo*-Phytosphingosine Derivative" *Tetrahedron Lett.* **2007**, *48*, 1105.

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E. Lee, K. Lee, S. Lee, S. Jung, J. Ha and C. H. Lee, “Manufacture of Supported Metallocene Catalysts and Polyolefins Therewith” International Patent Application 2006025709, March 9, 2006.