

Master's Thesis

Chemical Engineering

Ethylene polymerization and polyethylene functionalization

REPORT

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ABSTRACT - RESUMEN DE LAS PARTES DEL CONTENIDO DEL PROYECTO:

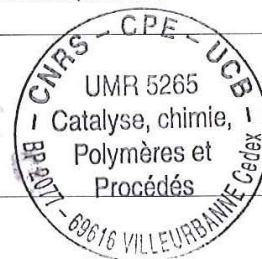
Polyolefins have become ubiquitous and are large volume commodity materials. Of current interest is the preparation of speciality polymers incorporating polyethylene (PE), which often requires polymer chain-end manipulation. Ethylene polymerization by a neodymium catalyst in conjunction with n-butyloctylmagnesium (BOMg) incorporates reversible chain-transfer between Nd (where PE chains grow) and Mg (where PE chains rest). Using a large BOMg/Nd ratio for ethylene polymerization leads to magnesium-bound PE chains (PE-Mg-PE). We showed PE-Mg-PE is a precursor to end functionalized PE (PE-X) the potential applications of which include the design of macromolecular architectures based on PE. A drawback of the polymerization system is the optimum operating temperature (80°C) which is sufficient to produce only low molecular weight PE. This study aims to develop a polymerization system in which reversible chain transfer occurs at a high operating temperature. A catalyst system based on a dichloro-iron(II)-2,8-bis(imino)quinoline complex, [(BIQ)FeCl₂], is a suitable candidate due to i) satisfactory polymerization behaviour above 100°C when activated by methylaluminoxane (MAO) and ii) the potential for chain transfer with ZnEt₂, established previously with Fe based catalysts. [(BIQ)FeCl₂] was assessed for ethylene polymerization in the absence and in presence of ZnEt₂.

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1. Abstract

Polyolefins have become ubiquitous and are large volume commodity materials. Of current interest is the preparation of speciality polymers incorporating polyethylene (PE), which often requires polymer chain-end manipulation. Ethylene polymerization by a neodymium catalyst in conjunction with *n*-butyloctylmagnesium (BOMg) is based on a reversible chain-transfer between Nd (where PE chains grow) and Mg (where PE chains rest). Using a large BOMg/Nd ratio for ethylene polymerization leads to magnesium-bound PE chains (PE-Mg-PE). We showed PE-Mg-PE is a precursor to end functionalized PE (PE-X) the potential applications of which include the design of macromolecular architectures based on PE. A drawback of the polymerization system is the optimum operating temperature (80°C) which is sufficient to produce only low molecular weight PE. This study aims to develop a polymerization system in which reversible chain transfer occurs at a high operating temperature. A catalyst system based on a dichloro-iron(II)-2,8-bis(imino)quinoline complex, [(BIQ)FeCl₂], is a suitable candidate due to i) satisfactory polymerization behaviour above 100°C when activated by methylaluminoxane (MAO) and ii) the potential for chain transfer with ZnEt₂, established previously with Fe based catalysts. [(BIQ)FeCl₂] was assessed for ethylene polymerization in the absence and in presence of ZnEt₂.



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3. Glossary

TBP	2,6-di-tert-butyl-phenol
BIQ	2,8-bis[1-(2,6-dimethylphenylimino)ethylquinoline]
MgR ₂	Dialkylmagnesium
CCG	Catalyzed Chain Growth
CSA	Chain Shuttling Agent
CTA	Chain Transfer Agent
CCTP	Coordinative Chain Transfer Polymerization
D _p	Degree of polymerization
C ₆ D ₆	Deuterated benzene
CDCl	Deuterated chloroform
CD ₃ OD	Deuterated methanol
(BPI)ZrBn ₂	Dibenzylzirconium bis (phenoxyimine)
(BIQ)FeCl ₂	Dichloroiron(II)-2,8-bis(imino)quinoline complex
Phoxim ₂ ZrCl ₂	Dichlorozirconiumbis(phenoxyimine)
ZnEt ₂	Diethyl Zinc
g	Gram
Hf	Hafnium
HDPE	High Density Polyethylene
h	Hour
H	Hydrogen
IR	Infrared



Fe(Bipy)	Iron (II) bis(imino)pyridine
LCPP	Laboratory for the Chemistry and Processes of Polymerization
LLDPE	Linear low density polyethylene
LDPE	Low density polyethylene
Mg	Magnesium
MAO	Methylaluminoxane
μM	Micromolar
mg	Miligram
MMAO	Modified methylaluminoxane
mM	Milimolar
M	Molar
M_i	Molecular weight of chains in fraction i
BOMg	<i>n</i> -butyloctylmagnesium
Nd	Neodymium
LnNd	Neodymium catalyst
NMR	Nuclear Magnetic Resonance
Mn	Number average molecular weight
Ni	Number of chains in fraction i
ppm	Parts per million
M_p	Peak molecular weight
Ph	Phenyl
PDI	Polydispersity Index



PE	Polyethylene
P	Pressure
rpm	Revolutions per minute
SEC	Size Exclusion Chromatography
T	Temperature
t-Bu	tert-butyl
THF	Tetrahydrofuran
Ti	Titanium
TiCl ₄	Titanium tetrachloride
AlEt ₃	Triethyl aluminium
TEA	Triethylaluminium
TMA	Trimethylaluminium
(C ₆ H ₅) ₃ C ⁺ (C ₆ F ₅) ₄ B ⁻	Trityl tetra(pentafluorophenyl)borate
Ph ₃ CB(C ₆ F ₅) ₄	Trityl tetrakis-(perfluorophenyl)borate
v/v	Volume fraction
M _w	Weight average molecular weight
W _i	Weight of chains in fraction i
%wt	Weight percent





4. Introduction

Polyethylene (PE) is a hydrocarbon polymer, produced globally on a large scale. The production of polyethylene has been a major area of research in chemistry and engineering during the 20th and 21st centuries..

Two main types of polyethylene are produced on a large-scale: the low density polyethylene (LDPE) and the high density polyethylene (HDPE). The former is amorphous and characterized by low molecular weights and branched chains, while the latter typically has higher molecular weights and linear chains, promoting crystallinity.

The synthesis of polyethylene is most commonly achieved by polymerization of ethylene using a catalyst, typically a metal complex, and a cocatalyst, used to activate the catalyst in order to initiate polymerization.

4.1. Thesis objectives

A dichloroiron(II)-2,8-bis(imino)quinoline complex, [(BIQ)FeCl₂], and a dibenzylzirconium bis (phenoxyimine) complex, [(BPI)ZrBn₂], were tested as ethylene polymerization catalyst. The main reason why the neodymium catalyst was changed it is due to the low range of temperatures that it allows to be used.

A test of other cocatalyst types, as methylaluminoxane (MAO) and diethyl zinc (ZnEt₂), was done in order to polymerize with the [(BIQ)FeCl₂] and the [(BPI)ZrBn₂]. Functionalized polyethylene was essayed to obtain at higher temperatures and also with lower molar mass polyethylene.

4.2. Thesis scopes

The [(BIQ)FeCl₂] precatalyst was synthesized and analyzed. Essays with this precatalyst were done in order to know the conditions of ethylene polymerization. The polyethylene obtained with [(BIQ)FeCl₂] complex, was analyzed and compared with the bibliographical one. Functionalization of the polyethylene obtained was carried out.

The second point covered was to find the polymerization conditions of [(BPI)ZrBn₂] using a borate cocatalyst. A chain shuttling agent was added to control polymerizing chains grow and those conditions were compared with the literature reported. Polymer properties were compared with the literature ones and to functionalize this polyethylene was also essayed.



5. Bibliographical research

5.1. Uses and properties of polyethylene

Polyethylene (PE) is a polymer with a wide range of applications, and its use is particularly prevalent in commodity applications such as packaging (film, bags, sealing, bottles, etc) due to its low production cost. The use of PE in piping and tubing highlights its strength and chemical resistant properties. Its ubiquity derives from its features: toughness, hardness, ease of processing, lack of toxicity and high impact resistance [1].

Polyethylene consists of long chains of covalently bound carbon atoms, each attached to a pair of hydrogen atoms. The average chain length can be expressed using the degree of polymerization (D_p) defined by the equation (1).

$$(1) \quad D_p = \frac{\text{Total molecular weight of the polymer}}{\text{Molecular weight of the monomer unit}}$$

The extent of chain branching in a sample of PE determines its density of the PE and its level of crystallinity. The lower the level of chain branching, the less intermolecular space exists and the more crystalline and dense the polymer is. On the other hand, the greater the level and size of chain branching, an increasingly amorphous and lower density polymer is encountered.

The polymerization degree can be extremely high, exceeding 3,500,000 [2] in some cases. During the polymerization of ethylene chains grow at different rates which results in a distribution of chain lengths and thus molecular weight. Several values can be calculated from the molecular weight profile to characterize the distribution [2] *Figure 1*:

\overline{M}_n : number average molecular weight which is calculated according to equation (2)

$$(2) \quad \overline{M}_n = \frac{\sum M_i \cdot N_i}{\sum N_i} = \frac{\sum W_i}{\sum N_i}$$

\overline{M}_w : weight average molecular weight which is calculated according to equation (3)

$$(3) \quad \overline{M}_w = \frac{\sum M_i^2 \cdot N_i}{\sum M_i \cdot N_i} = \frac{\sum M_i \cdot W_i}{\sum W_i}$$

M_p : peak molecular weight, which is the maximum molecular weight of a molecular weight distribution plot (*Figure 1*).



Polydispersity Index (PDI): A quantitative description of the molecular weight distribution and it is calculated as shown in equation (4).

$$(4) \quad PDI = \frac{M_w}{M_n}$$

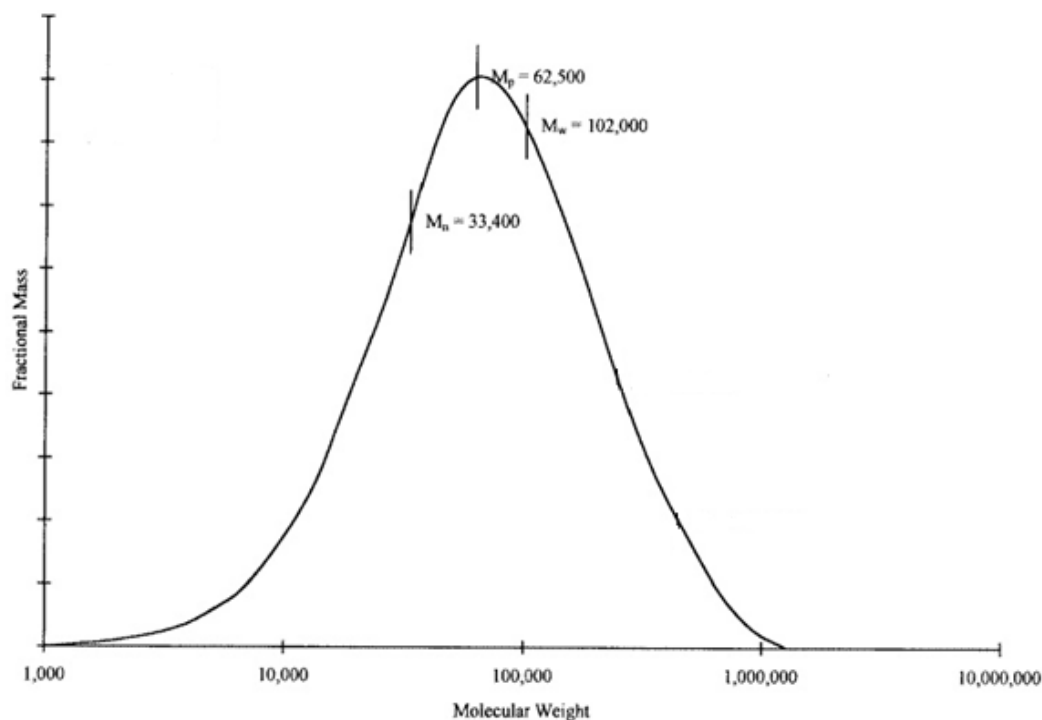


Figure 1 : Typical molecular weight distribution plot of polyethylene [2]

5.2. PE synthesis

Polyethylene is synthesized on a commercial scale by the polymerization of ethylene. Depending on the method of polymerization, different types of polyethylene are accessible: low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE).

LDPE is produced traditionally by free radical polymerization. This process requires a radical initiator, commonly oxygen, an organic peroxide or azo compound, and is performed at high pressure and temperature. Typical ranges of the reactor pressure are 1000-1550 bar and range of temperature between 100-300°C [2]. Under high pressure initiator molecules are decomposed producing free radicals. Propagation occurs by radical addition to ethylene, while the radical chain end may engage in intramolecular or intermolecular hydrogen abstraction from the interior of a chain, causing chain branching



and resulting in production of LDPE. HDPE and LLDPE are prepared by catalytic polymerization, with commercial processes using e.g. Ziegler-Natta and Phillips catalysts (*Figure 2*). Ziegler-Natta polymerization is a low pressure, a range of pressure from 1bar to 21bar [2], way of producing polyethylene.

Cr OXIDE CATALYSTS

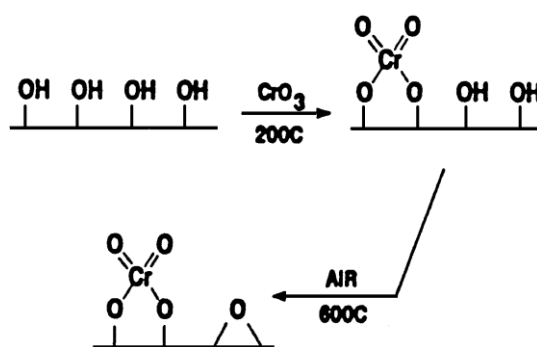


Figure 2: Phillips catalyst. Steps in the formation of an olefin polymerization catalyst

The first effective production of HDPE was done by Karl Ziegler in 1957 using a metal catalyst. Ziegler-Natta catalysts consist of a group I-III metal alkyl or halide with a transition metal (groups IV-VIII from the periodic table) complex. The Ziegler-Natta catalysts used in solution polymerization are soluble, homogeneous catalysts, while those used in gas-phase reactors are supported on materials such as silica for heterogeneous catalysis.

An example of a Ziegler-Natta catalyst which polymerizes ethylene to HDPE is the combination of triethyl aluminium (AlEt_3) with titanium tetrachloride (TiCl_4). The mechanism, elucidated by Cossee and Arlman [3] is showed on *Figure 3*. The titanium centre is activated by abstraction of chloride ligands and exchange for an ethyl ligand, as well as generation of a vacant coordination site. Ethylene then occupies the coordination site, and is subsequently inserted across the Ti-alkyl bond, extending the chain and regenerating a vacant coordination site. Propagation proceeds by this mechanism to produce polyethylene chains (*Figure 3*).

Metallocene complexes have been popular and effective catalysts for ethylene polymerization since Kaminsky's use of zirconocene in combination with Methylaluminoxane (MAO) as cocatalyst [4]. A cocatalyst is required to activate the metallocene complex towards ethylene polymerization, by generating a vacant coordination site and often to supply an alkyl initiating group. Methylaluminoxane (MAO) has proved particularly effective in both the range of precatalysts it is able to activate and the polymerization rates it has facilitated.



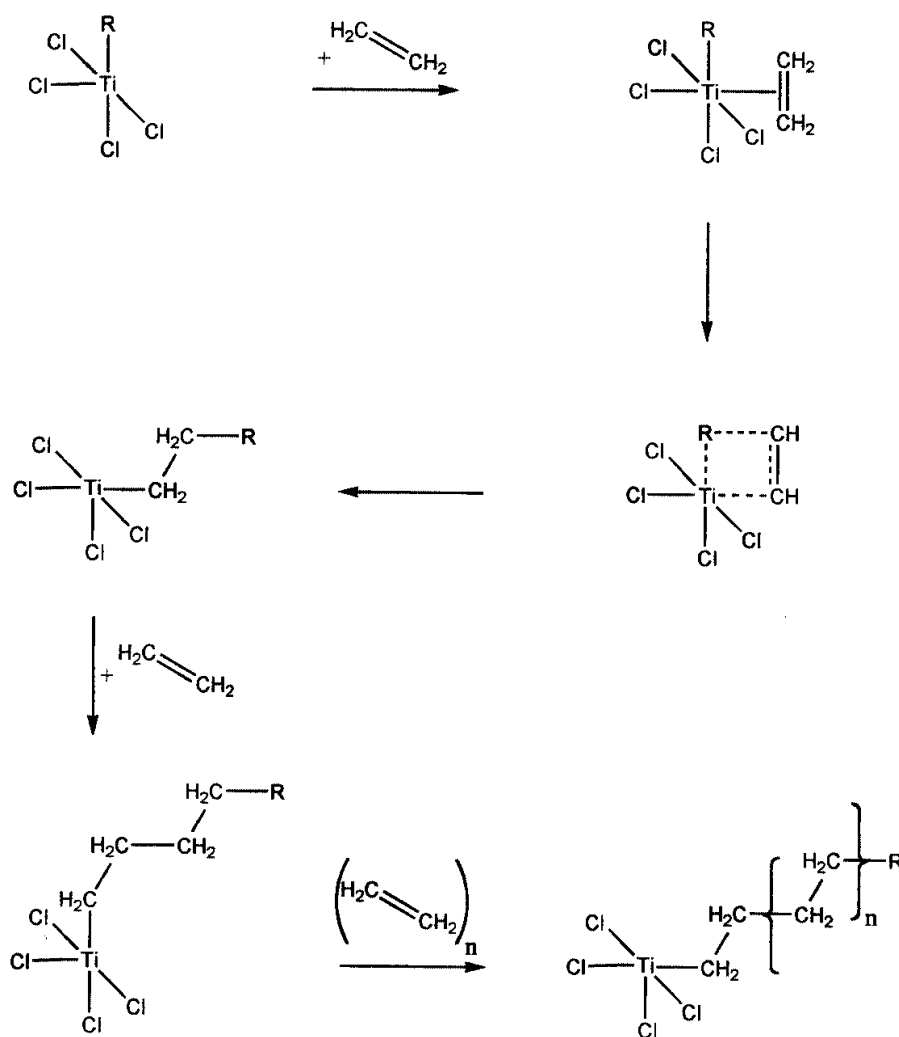
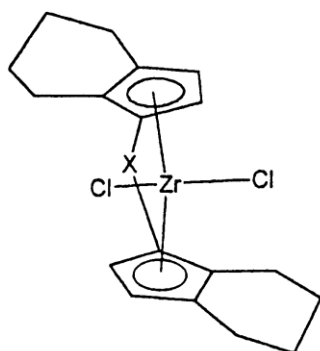


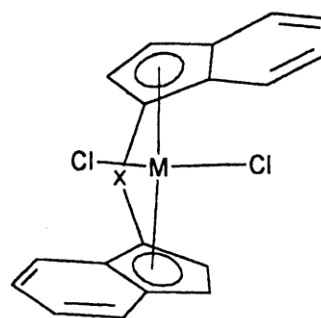
Figure 3: Cossee Arlman mechanism

Metallocene catalysts feature metal centers bound to multidentate, aromatic carbocycles, with halide ligands where required to ensure a neutral complex. The most commonly used metallocene catalysts involve a metal atom of group IV of the periodic table (titanium, zirconium or hafnium) attached to two substituted cyclopentadienyl ligands and two alkyl, halide or other ligands, combined with a methylaluminoxane cocatalyst. Substituents such as alkyl groups or bridging groups are generally attached to cyclopentadienyl ligands in order to control the polymerization behavior. Some examples of metallocene precatalyst which polymerizes ethylene are shown in *Figure 4*.

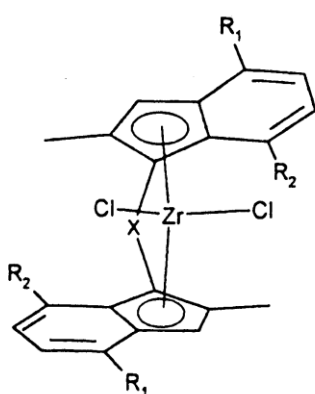




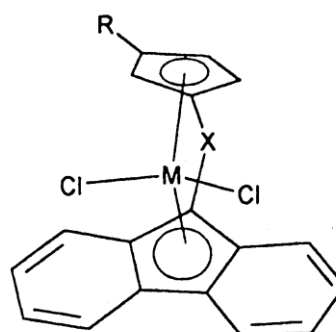
$X = C_2H_4, Me_2Si$



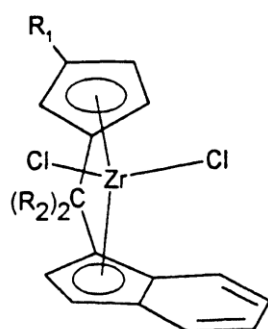
$M = Zr, Hf$
 $X = C_2H_4, Me_2Si$



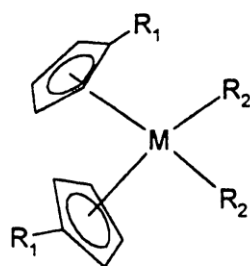
$X = C_2H_4, Me_2Si$
 $R_1 = Me, Ph, Naph$
 $R_2 = H, Me$



$M = Zr, Hf$
 $X = Me_2C, Ph_2C$
 $R = H, Me, t-Bu$



$R_1 = H, Me$
 $R_2 = Me, Ph$



$M = Ti, Zr, Hf$
 $R_1 = H, 5-Me, neomenthyl$
 $R_2 = Cl, Me$

Figure 4: Examples of metallocene precursor [4]

The polymerization mechanism for metallocene catalysts closely resembles that for Ziegler-Natta catalysts, involving halide abstraction and alkylation of the catalyst metal centre, followed by ethylene coordination and insertion into the M-alkyl bond (Figure 5).



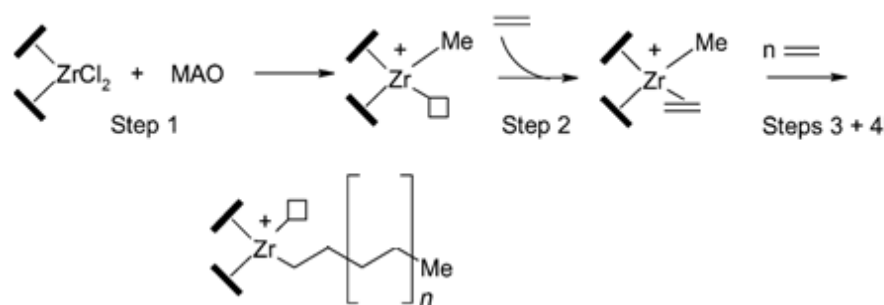


Figure 5: Mechanism of the polymerization of polyethylene by zirconocene complex [6]

In [4] Kaminsky reported the activities and the molecular masses of ethylene polymerization for different types of metallocene catalyst based on Hf, Zr and Ti activated with MAO. Zirconium containing catalysts were proved to be more active than Ti and Hf. Some examples of activities for bis(cyclopentadienyl)metal dichloride, the metallocene complex is shown at the right bottom in Figure 4, for metals are: Zr: 6,09, Ti: 3,42 and Hf: $0,42 \cdot 10^{-4} \frac{\text{Kg PE}}{\text{mol}_{\text{metallocene}} \cdot \text{h} \cdot \text{C}_{\text{ethylene}}}$. Kaminsky also reported that molecular masses for this type of metallocene were higher for Hf than Zr and the smallest molecular mass which was reported was for the Cp_2TiCl_2 complex, examples for the Cp_2MCl_2 are: 7 for Hf, 6,2 for Zr and 4 for the Ti $\cdot 10^{-5}$ g/mol.

After first metallocene compounds were discovered new families of catalyst have been found including complexes of nickel, palladium, iron and cobalt with MAO as cocatalyst. The most popular metallocenes are the group 4 and lanthanides.

An example of a lanthanide complex used as a homogeneous precatalyst was reported by Espinosa et al. [5]. A neodymium complex, L_nNd , in conjunction with BoMg , as cocatalyst, was used to synthesize polyethylene. This reaction is further explained in section 5.4.

5.3. Transfer mechanisms

Polymerizations of olefins are often accompanied by side reactions, such as polyolefin transfer mechanisms which may modify the nature of the polymer.

5.3.1. Hydrogenation

The control of molecular weight of Ziegler Natta catalysis is generally performed using hydrogen which leads to hydrogenation of the metal-carbon bond of the growing polymer



chain. A study about metallocene complexes, which was done by Helmut et al. [6], proposed the mechanism when hydrogen is supplied while polymerization takes place, this mechanism is shown in *Figure 6*.

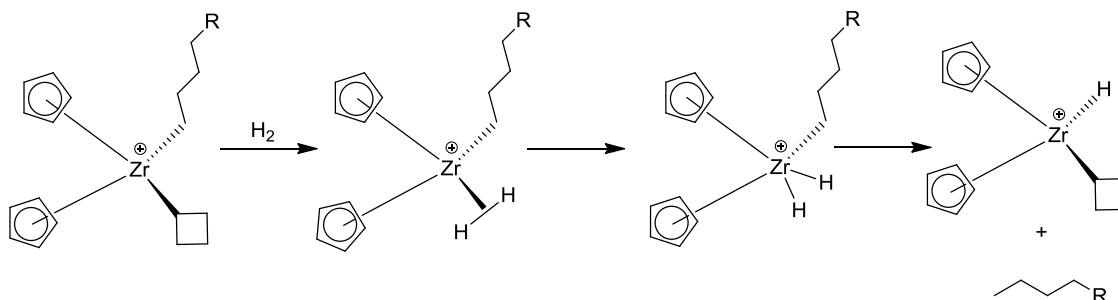


Figure 6: Transfer mechanism reaction with hydrogen

Polymer chain is detached from the metallocene complex and a hydride complex is formed which can initiate another polymer chain. The hydrogen addition to the polymerization is understood as a catalyst activity raise and also in a decrease in the molecular weight of the polyolefin.

5.3.2. β -hydride elimination

Unimolecular hydrogen transfer, *via* β -hydride elimination, causes the termination of polymer chain growth and produces a metal hydride and a vinyl-terminated polymer chain, a scheme of the β -hydride transfer reaction is shown in *Figure 7*. In some cases, the vinyl-terminated polymer can be inserted into another growing chain, producing a branched polymer.

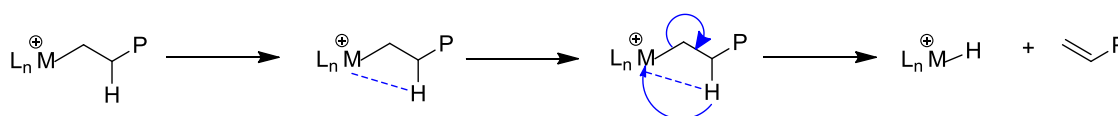


Figure 7: β -hydride transfer reactions. A hydrogen atom of the carbon in β position of the chain is transferred to the transition metal leading to a vinyl terminated polyolefin.

The rate of β -hydride transfer with respect to propagation rate is one factor determining the molecular weight and polydispersity of the polymer produced [7]. Typically, a high rate of β -hydride transfer will result in a low molecular weight with a broad molecular weight distribution. Control of molecular weight and limiting the polydispersity requires



minimization of termination reactions such as β -hydride transfer.

5.3.3. Chain transfer to metal

When a catalyst is used in combination with an alkyl aluminum cocatalyst, a chain transfer of the polymer chain to the aluminum is usually observed. As is shown in *Figure 8*, it is an exchange between the growing polymer attaches to the active chain with the alkyl groups attached to the alkylaluminum.

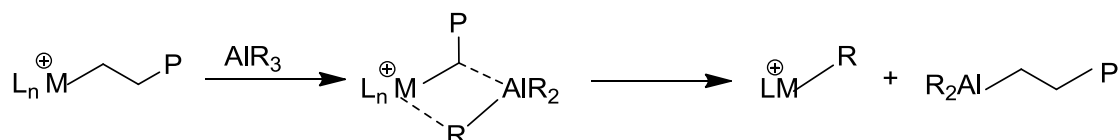


Figure 8: Chain transfer to aluminium

Chain transfer to aluminum in ethylene polymerization has been studied for many different catalyst systems across the transition metals, as well as lanthanides and actinides.

This chain transfer process is not limited to aluminum alkyls, indeed effective chain transfer has been achieved using beryllium ($BeEt_2$), magnesium (MgR_2) and zinc and cadmium alkyls (ZnR_2 and CdR_2) as CTAs [8].

5.3.4. Coordinative Chain Transfer Polymerization (CCTP)

When chain transfer to metal is the only chain transfer and also is fast (faster than propagation) and reversible it is named coordinative chain transfer polymerization (CCTP). The reaction mechanism is shown in *Figure 9*.

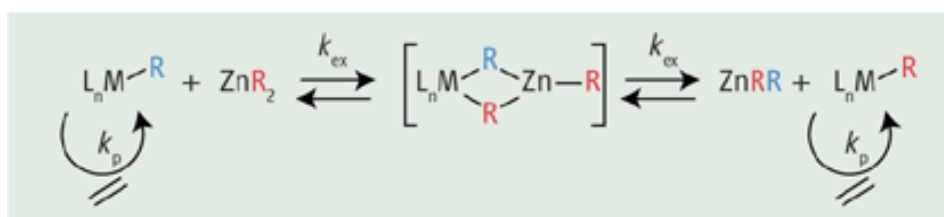


Figure 9: Catalyzed Chain transfer polymerization mechanism



CCTP polymerization system is also known as catalyzed chain growth (CCG) as the transition metal catalyses the apparent PE chain growth on a main group metal, the reaction is shown in *Figure 10*.

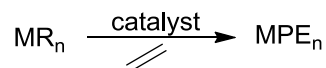


Figure 10: Catalyzed chain growth scheme

This concept of CCG was outlined by Gibson [9] with the synthesis of iron-catalyzed polyethylene with chain growth on zinc. Diethyl zinc (ZnEt_2), which has been used with Ziegler-Natta catalyst to control the molar mass and the chain end of the polyolefin through chain transfer to the Zn, is among the most efficient chain-transfer agents (CTA), due to a close matching of the metal-carbon bond energies of the zinc alkyl and the transition-metal alkyl species.

The chain transfer of the growing polymer chain to a metal can be exploited for three possible purposes: 1) to control the molecular weight, 2) to transfer chains between two catalysts and 3) to functionalize the polyethylene chain end.

When two different catalysts, each capable of polymerizing a different monomer, are used in a same polymerization with a chain-transfer agent, interesting copolymer structures may be accessible. Arriola et al. [10] developed a technique to produce linear multiblock copolymers which alternated hard and soft blocks, arising from chain shuttling between the two catalyst centers (*Figure 11*). Diethylzinc in this example is described as a chain-shuttling agent (CSA).

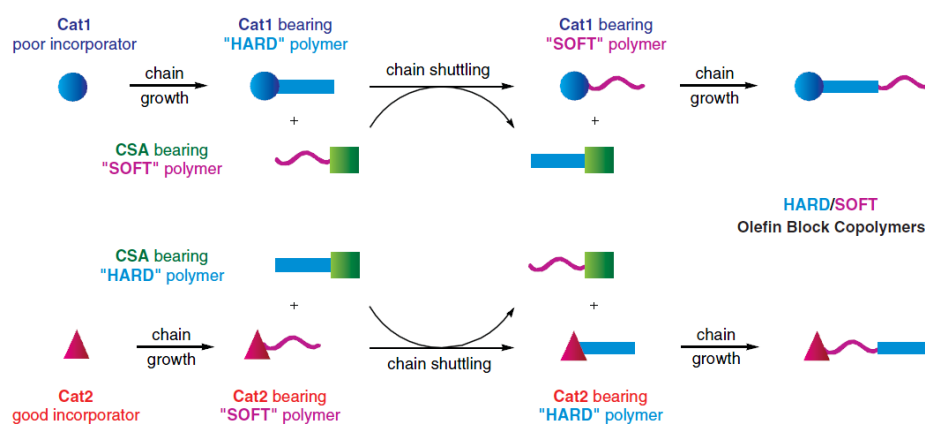


Figure 11: Chain shuttling mechanism reported by Arriola et al. for copolymer production



5.4. Functionalization of polyethylene

In general, functionalized polyolefin can be prepared by modification of a polyolefin containing an existing functional group, copolymerization of olefins with a functional monomer or by reaction of CTA-bound polymer chains with an electrophile directly following the polymerization. In this work the focus is on the latter method.

Espinosa et al. [5] have reported the synthesis of polyethylene building blocks by using a lanthanide metallocene catalyst and di-alkylmagnesium, acting both as an activator and as a CTA. The CCG mechanism between the butyloctylmagnesium cocatalyst (MgR_2) and the neodymium catalyst (L_nNd), shown in *Figure 12*, results in magnesium-bound polymer chains, $(\text{Mg})\text{PE}_2$.



Figure 12: Nd catalyst used with di-alkylmagnesium organometallic species as CTA

Figure 13 shows the polymerization of ethylene to produce end-functionalized polyethylene. One that functionalized polyethylene was fully performed a reaction with iodide to produce iodopolyethylene (PE-I) was done.

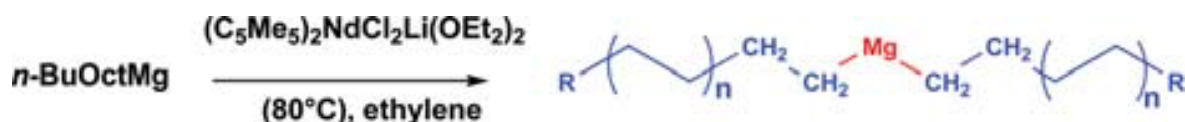


Figure 13: Production of $\text{Mg}(\text{PE})_2$ with neodymium catalyst

An impediment to obtaining high molecular weight functionalized polymers using the Nd / Mg system is that above 80°C , chain termination reactions increase markedly, compromising product yield, while only low molecular weight polyethylene remains soluble at 80°C . The aim of this project is to extend the ability to obtain functionalized polyethylene in high yield to high molecular weight PE, by performing controlled CCTP at high temperatures.



6. Ethylene polymerization with [(BIQ)FeCl₂] complex

6.1. Introduction

Iron complexes are often used as catalyst for ethylene polymerization because of iron's low cost and availability.

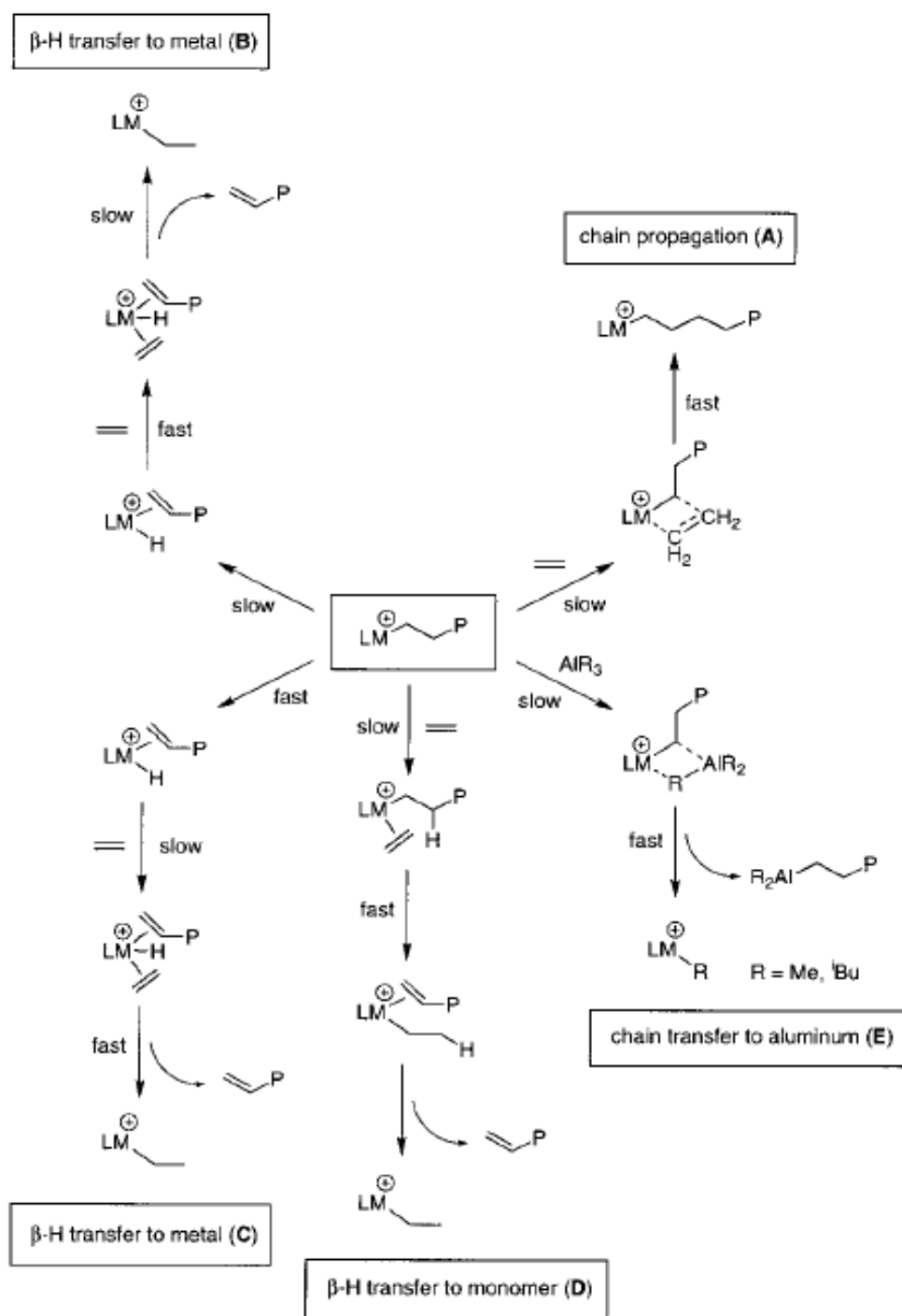
Polymerization of ethylene using an iron complex bearing 2,6-bis(imino)pyridyl ligands was reported by Britovsek et al. in 1998 and 1999 [11]-[12]. Ethylene polymerization with these iron complexes was done with MAO as activator at 25°C and 50°C temperatures and pressures between 1 and 10 bar. Under these conditions mainly HDPE was obtained with an activity range from 120 to 20000 g/mmol·h·bar.

The processes occurring during the polymerization were propagation, β -hydrogen transfers, as well as chain-transfer between the Fe and Al centers (*Scheme 1*). Later studies such as by Bryliakov et al. [13][12], investigated the mechanism of ethylene polymerization using iron (II) and iron (III) bis(imino)pyridine catalysts in the presence of MAO.

Britovsek et al. [12] studied the chain growth of an iron catalyzed polyethylene on zinc. An iron (II) bis(imino)pyridine complex, shown in *Figure 14*, was used in combination with MAO and ZnEt₂. The high propagation rate for this system was complimented by rapid, reversible alkyl exchange between iron and zinc. This catalyzed chain growth reaction produces linear alkanes with a Poisson molecular weight distribution.

Zhang and coworkers [14] in 2010 reported the synthesis of an iron complex which was able to polymerize ethylene at higher temperatures than the iron bis(imino)pyridine complexes. No activity at ambient temperature is shown by iron bis(imino)quinoline complexes but at high reaction temperature (80-100°C) a polyethylene with narrow molecular weight distribution is produced. By increasing ethylene pressure higher activities were observed, lower polyethylene molecular weights were obtained along with narrower molecular distribution.





Scheme 1: Possible chain propagation and transfer pathways for ethylene polymerization with iron pyridine complexes



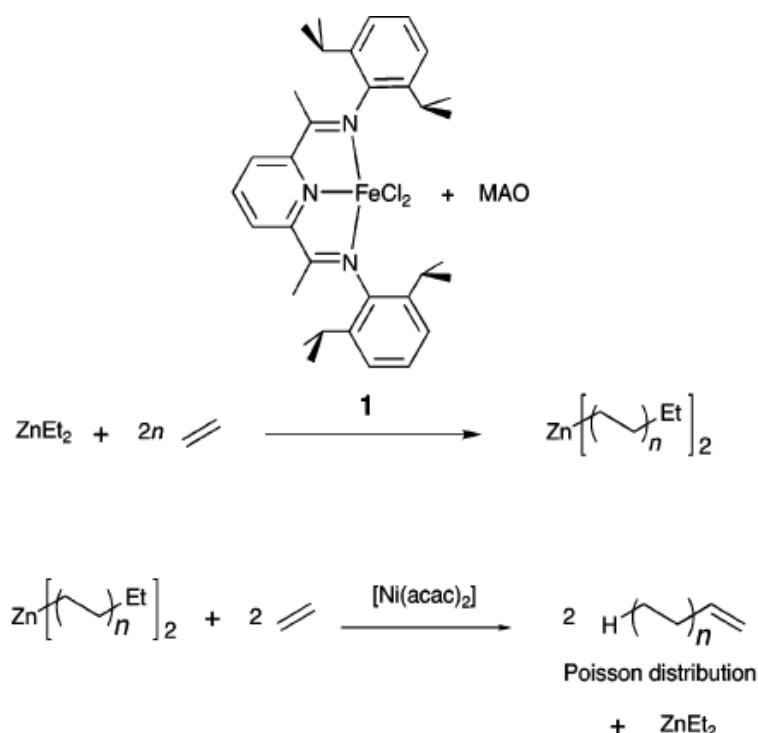


Figure 14: iron catalyzed chain growth of polyethylene on zinc

In this report a similar iron bis(imino)quinoline complex is prepared and used for the polymerization of ethylene with MAO as a cocatalyst. The results obtained are compared with literature precedents, and the conditions for optimal polymerization behavior investigated. The ability of this catalyst to undergo chain transfer was studied by the introduction of the potential chain transfer agent diethylzinc.

6.2. Experimental section

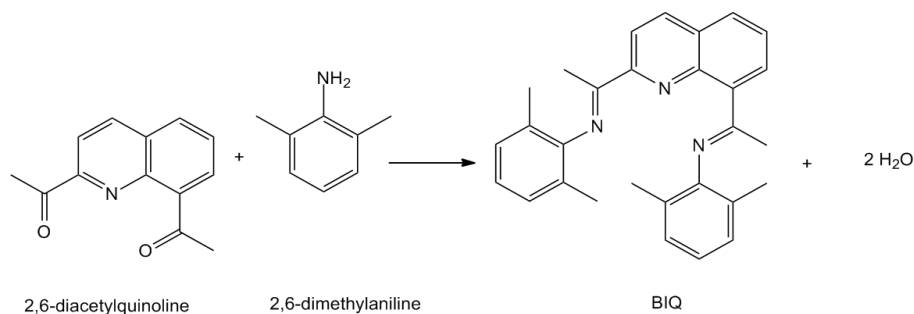
6.2.1. General considerations

All manipulations of oxygen and moisture sensitive compounds were performed under argon atmosphere using standard Schlenk techniques. Dried toluene, tetrahydrofuran and diethyl ether are extracted from the MBraun-SPS 800 fountain solvent. 2,8-diacetylquinoline was supplied by Zhang and co-workers [14]. 30% wt MAO in toluene was purchased from Aldrich and diluted to a 10% solution. All other chemicals were purchased from Aldrich or Acros Chemicals. ^1H nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance II 250 spectrometer operating at 250MHz. Infrared analyses (IR) was performed on a Nicolet iS10 spectrometer. PE molecular weights were determined by size exclusion chromatography (SEC) using a Waters Alliance GPCV 2000 instrument.



6.2.2. Synthesis of 2,8-Bis[1-(2,6-dimethylphenylimino)ethylquinoline]

The proligand 2,8-bis[1-(2,6-dimethylphenylimino)ethylquinoline], [BIQ], was synthesized as reported by Zhang et al.[14], (*Scheme 2*), by condensation of 2,6-diacetylquinoline with 2 equivalents of 2,6-dimethylaniline. Purification was achieved by chromatography using a basic alumina stationary phase and ethyl acetate/petroleum ether (10:1 v/v) as eluent, followed by recrystallization from pentane. The yield obtained was 28,7%.

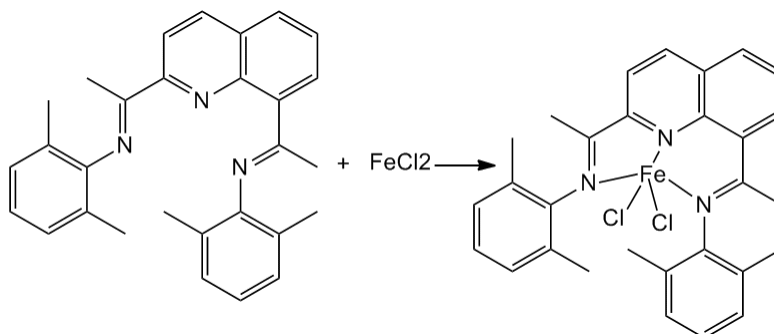


Scheme 2: Synthesis of the ligand 2,8-bis[1-(2,6-dimethylphenylimino)ethylquinoline], [BIQ]

The bis(imino)quinolone proligand was characterized by ¹H NMR and IR spectrometry. The spectra obtained are displayed in the appendix (*section 10*).

6.2.3. Synthesis of dichloro-iron(II)-2,8-bis(imino)quinoline complex [(BIQ)FeCl₂]

The synthesis of (BIQ)FeCl₂ complex was performed using a similar procedure to that described by Zhang et al. [14] (*Scheme 3*), however anhydrous iron (II) chloride was used instead of iron (II) chloride pentahydrate. The complex (BIQ)FeCl₂ was obtained as a green powder in 44% yield, and was stored under argon in a glove box.



Scheme 3: Reaction for the synthesis of (BIQ)FeCl₂ complex

The ¹H NMR spectra is shown in the section 6.3.



6.2.4. Ethylene polymerization

Two reactors were used, a 1000ml metallic reactor (*Figure 15*) and a 500 ml glass reactor (*Figure 16*). Both of them had argon supplying and ethylene ballast was directly connected to each one of them.

Two solutions were prepared in separate Schlenk flasks under Ar atmosphere. One Schlenk contained (BIQ)FeCl₂, introduced inside the glove box, in toluene. The other Schlenk contained a solution of MAO in toluene. A triethylaluminium (TEA; 5 mM) solution in toluene was used to clean the reactor, followed by dried toluene, to remove alkylaluminium residues. The (BIQ)FeCl₂ suspension was introduced by cannulation under an argon or ethylene atmosphere. Then MAO/toluene solution was then introduced, also under argon or ethylene atmosphere by the cannule inlet which is shown in *Figure 15*. The reagents were stirred at 600 rpm, and heated to the desired polymerization temperature, whereupon then pressure of ethylene was adjusted to the desired pressure.

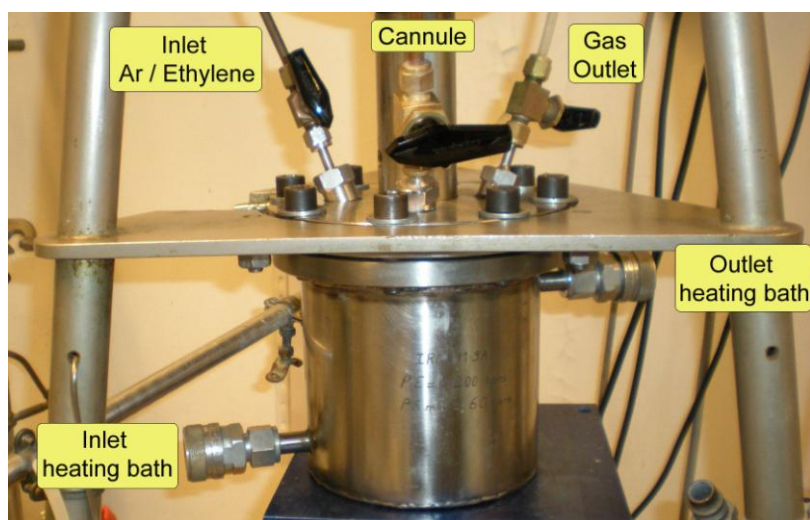


Figure 15: Metallic reactor



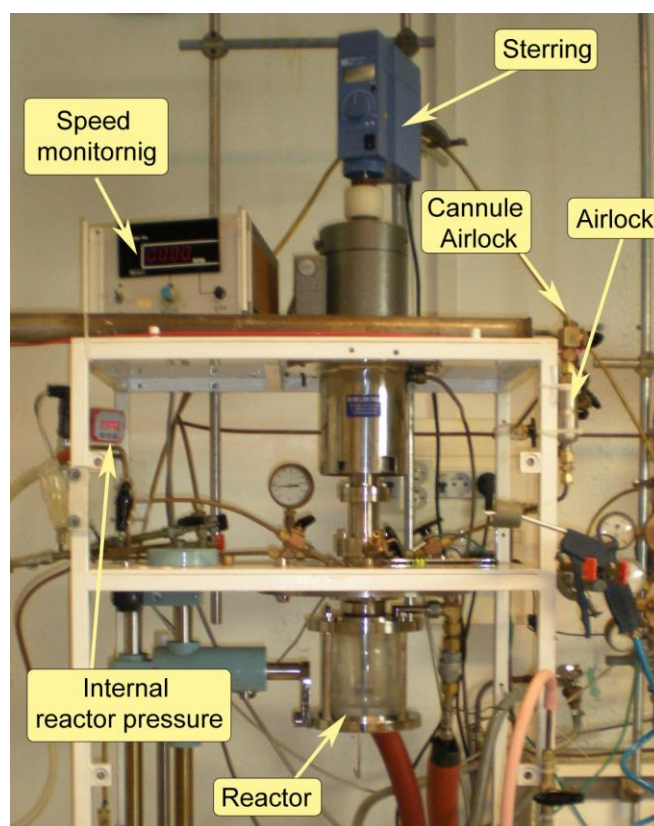


Figure 16: Glass reactor

When the ethylene flow was cut, excess pressure was evacuated by opening the gas outlet valve. The solution inside the reactor was cooled down ethanol quenching was done in order to react the excess of MAO and can open it to the atmosphere. The polymer was cleaned with acidic ethanol and filtered. After with ethanol it was cleaned and filtered too in order to remove the acidic ethanol. Finally the polyethylene was dried.

6.2.5. Molecular weight control by CCTP

The experiences were carried using ZnEt_2 and BoMg as a possible CTA.

Two solutions were prepared in separate Schlenk flasks under Ar atmosphere. One Schlenk contained $(\text{BIQ})\text{FeCl}_2$, introduced inside the glove box, in toluene. The other Schlenk contained a solution of MAO and CTA in toluene, CTA was first added and then the MAO inside the flask. A triethylaluminium (TEA; 5 mM) solution in toluene was used to clean the reactor, followed by dried toluene, to remove alkylaluminium residues. The $(\text{BIQ})\text{FeCl}_2$ suspension was introduced by cannulation under an argon or ethylene atmosphere. Then MAO/CTA/toluene solution was then introduced, also under argon or ethylene atmosphere. The reagents were stirred at 600 rpm, and heated to the desired



polymerization temperature, whereupon then pressure of ethylene was adjusted to the desired pressure.

The same procedure before opening the reactor and to clean the polymer was made as in section 6.2.4

6.3. Results and discussion

The complex (BIQ)FeCl₂ was prepared by stirring an ether solution of bisiminoquinoline with anhydrous iron (II) chloride, and isolated as a green powder. The ¹H NMR spectrum of (BIQ)FeCl₂ is shown in Figure 17, The five aromatics protons of the quinoline appear as doublets from 8,45ppm until 7,73ppm. The six other aromatics protons of the aniline appear as triplets and quadruplets at 7,04 and 6,9ppm. Finally the 18 protons of the methyl groups appear from 2,31ppm until 1,97ppm.

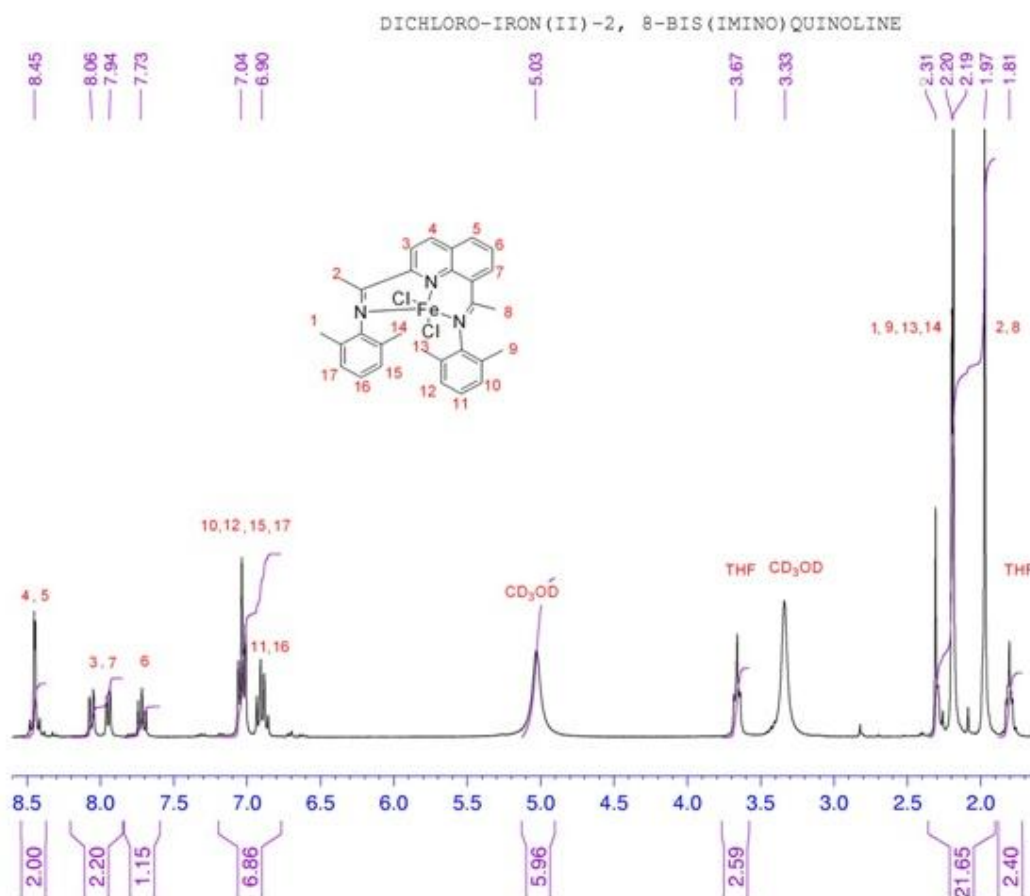


Figure 17: ¹H NMR spectra at room temperature in CD₃OD.



A series of experiments for ethylene polymerization using (BIQ)FeCl₂ were run. *Table 1* shows the results of those run in a glass reactor, *Table 2* shows the experiments run in a metallic reactor and *Table 3* shows the experiments when trying to control the molecular weight of the polymer obtained.

Experiments 4 (*Table 1*) and 10 (*Table 2*) used modified methylaluminoxane (MMAO) as a cocatalyst, prepared by stirring MAO for 30min with 0,5 equivalents of 2,6-di-tert-butyl-phenol (TBP), to ensure that no residual trimethylaluminium (TMA) was present in the MAO solution (the quantity of TBP used was the calculated from the estimated TMA content of the MAO solution and 2 moles of TBP were used for each mole of TMA).

The cocatalyst and the catalyst solutions in runs 9 and 10 from *Table 2*, were introduced inside the reactor under ethylene atmosphere while in all others runs they were introduced under an argon atmosphere.

In experiment 11 (*Table 3*) ZnEt₂ was used as a chain-transfer agent (CTA) while in experiment 12 (*Table 3*) butyloctylmagnesium (BOMg) was introduced to act as a CTA. For the purposes of calculating activities, the time period of the polymerization was assumed to be 20seconds.

Molecular weights (M_n) and molecular weight distributions were estimated using SEC. The chromatograms for each experiment (1-12) are shown in the appendix (*section 10.3*).



Experiment	P (bar)	T(°C)	(BIQ)FeCl ₂ (μM)	Mol MAO/(BIQ)FeCl ₂	Yield (mg)	Activity (g/mol*h*bar)	M _n (g/mol)	PDI	Mol PE obtained	Mol PE obtained / mol (BIQ)FeCl ₂
1	6	78,6	-	-	0	-	-	-	-	-
2	6	78,6	140	290	154	1100	81772	2,3	1,9E-06	0,01
3	4	100	67	1100	44	7400	40279	1,8	1,1E-06	0,05
4	4,85	85	50	850	533	3100	118240	1,8	4,5E-06	0,23

Table 1: Ethylene polymerization in glass reactor

Experiment	P (bar)	T(°C)	(BIQ)FeCl ₂ (μM)	Mol MAO/(BIQ)FeCl ₂	Yield (mg)	Activity (g/mol*h*bar)	M _n (g/mol)	PDI	Mol PE obtained	Mol PE obtained / mol (BIQ)FeCl ₂
5	20	90	-	-	41	-	61	12	6,7E-04	-
6	22	95	67	1100	225	1000	49296	2,2	4,6E-06	0,23
7	22	95	67	3400	1176	900	50449	2,2	2,3E-05	1,17
8	20	90	46	1200	630	1500	98290	1,8	6,4E-06	0,21
9	22	96	50	1200	4360	9300	107734	1,9	4,0E-05	1,35
10	20	96	50	1100	5304	13600	112864	1,8	4,7E-05	1,57

Table 2: Ethylene polymerization in metallic reactor

Experiment	P(bar)	T(°C)	(BIQ)FeCl ₂ (μM)	Mol MAO/(BIQ)FeCl ₂	Mol CTA/(BIQ)FeCl ₂	Yield (mg)	Activity (g/mol·h·bar)	M _n (g/mol)	PDI	Mol PE obtained	Mol PE obtained / mol (BIQ)FeCl ₂
11	22	96	50	1207	60	300	$5,43 \cdot 10^7$	6267	18,2	4,77E-08	3,18E-03
12	22	96	50	1207	1	150	$2,70 \cdot 10^7$	42313	3,9	3,5E-09	2,34E-04

Table 3: Ethylene polymerization and CCTP in glass reactor

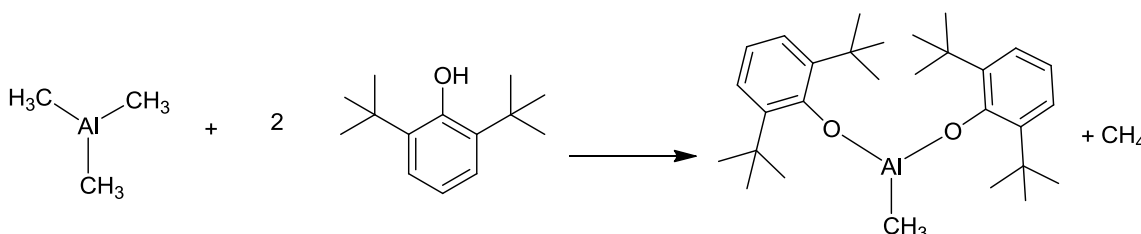
Experiments 2 to 4 (*Table 1*) were run at low pressure and high temperature, from 4 to 6 bar and from 78 to 100°C, and with molar ratios between MAO, used as cocatalyst, and (BIQ)FeCl₂ from 290 to 1100. In all experiments polymerization activities were low: from 1100 to 7400 g/mol·h·bar. The yield of polyethylene obtained was also low, from 44 to 533 mg of polyethylene with a M_n coming from 82000 to 118000 g/mol with a narrow range of PDI, from 1,8 to 2,3.

In experiments 6 to 10 (*Table 2*) MAO was used as cocatalyst with ratios between MAO/(BIQ)FeCl₂ from 1100 to 3400. The catalyst is active for ethylene polymerization and polyethylene was produced with M_n from 49000 to 113000 and with PDI remaining relatively constant from 1,8 to 2,2. The system which shows a peak activity are the conditions of run 10 (13600 g/mol·h·bar)

Experiments 9 and 10 (*Table 2*) are at high pressure and high temperature with MAO/(BIQ)FeCl₂ ratio of 1200 and 1100 respectively. Ethylene was polymerized with activities of 9300 and 13600 g/mol·h·bar respectively.

When a CTA was added, experiments 11 and 12 (*Table 3*), ethylene consumption stops abruptly after the polymerization and only traces of polymer were obtained. In both cases polymerization were run at high pressure and temperature, 22 bar and 96°C, with MAO used as cocatalyst in a molar ration with (BIQ)FeCl₂ of 1207.

Busico et al. [15] in 2003 studied the effect of the AlMe₃ (TMA) contained in commercial MAO, and demonstrated that TMA affects to the activity of the polymerization more than chain transfer. Busico and coworkers studied a way of deactivating TMA in the polymerization; 2,6-di-tert-butyl-phenol was added in order to react with TMA and Al(Me)(2,6-di-tertbutylphenoxide)₂ was proposed to be formed as shown in *Scheme 4*.



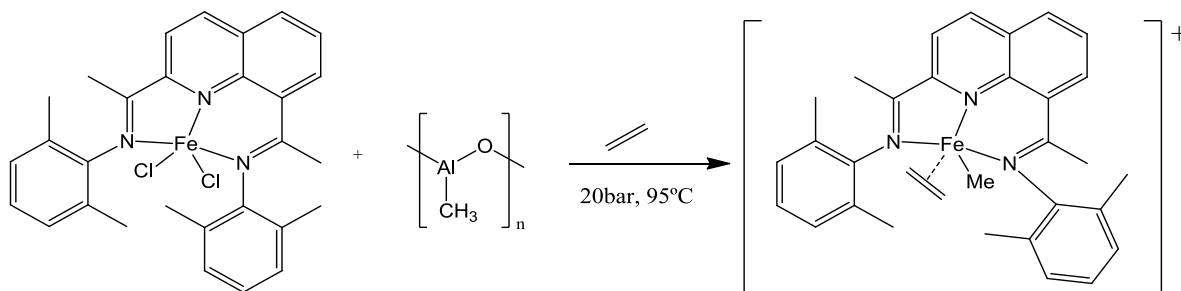
Scheme 4: Reaction between TMA from MAO and TBP to form Al(Me)(2,6-di-tertbutylphenoxide)₂.

In experiment 4, *Table 1*, no increase on the activity of the polymerization is observed compared to experiment 3 which has been run with similar conditions. Similarly, in run 10, *Table 2*, no substantial increase in activity is observed compared to run 9 which has similar



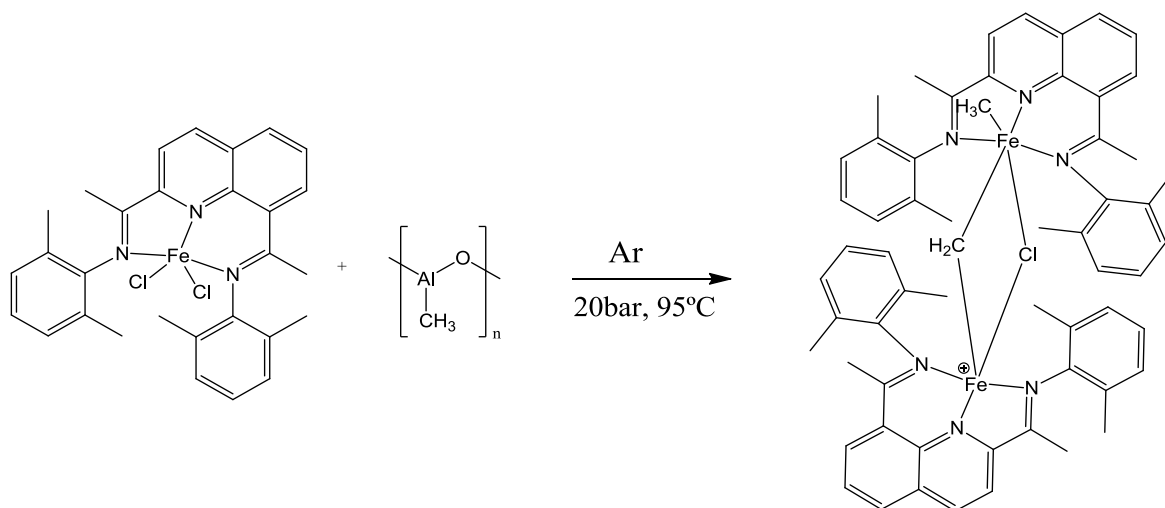
operational conditions. Experiments 9 and 10 show activities similar to those reported in the literature.

Another interesting feature is that the introduction of the catalyst and cocatalyst under argon atmosphere results in little or no polymerization activity, while introduction under an ethylene atmosphere allows polymerization to proceed. A possible explanation may be the formation of aggregates, inactive towards ethylene polymerization, by the iron species upon alkylation, a reaction which is inhibited by the presence of ethylene (Scheme 5).



Scheme 5: Desired polymerization reaction with (BIQ)FeCl₂. Proposed activation and initiating species

The fact that this effect was not observed with activation of the iron (II) bis(imino)pyridine precatalyst, Fe(Bipy), could be due to the relative strengths of the ligand-metal bonds. The iron-nitrogen bonds from the Fe(Bipy) complex have a smaller distance than the same bonds of the (BIQ)FeCl₂ complex. A possible aggregation product is illustrated in *Scheme 6*.



Scheme 6: Possible reaction between (BIQ)FeCl₂ complex and MAO under Ar atmosphere



Catalyzed chain-transfer polymerization (CCTP) is a desirable target due to the potential control available over molecular weight and end-group functionality. In run 11 polymerization of ethylene was attempted using the complex (BIQ)FeCl₂, MAO and diethylzinc, introduced as a proposed chain-transfer agent (CTA).

When ZnEt₂ was used as CTA (run 11), in a molar ratio with the iron complex of 60, the ethylene polymerization activity was very high ($5,43 \cdot 10^7$ g/mol·h·bar) and the polyethylene was produced (300mg) with a M_n of 6267 g/mol and with a PDI of 18,2.

When BOMg was used as CTA (run 12), in a molar ratio with the iron complex of 1, the ethylene polymerization activity was $2,7 \cdot 10^7$ g/mol·h·bar and the polyethylene was produced (150mg) with a M_n of 42313 g/mol and with a PDI of 3,9.

Comparing CTA polymerizations (*Table 3*) with run 9 (*Table 2*), which has nearly the same molar ratio between the cocatalyst and the catalyst and also the same operational conditions, an increase of the activity for both experiments with CTA, a decrease of the M_n and an increase of the PDI is observed.

Observing the number of chains of polyethylene produced for the run 11, which is 850 times lower than in run 9, means that chain transfer is taking place between the diethylzinc and the polyethylene. The increase of the PDI in 10 times in the run 11 in front of the run 9, is a symptom of the propagation going faster than chain transfer which may be affecting the initiation of the polymerization resulting in a reduction of the chain transfer. So in this case no CCTP is taking place because of the lack of fast polyethylene chain growth on Zn. The presence of ZnEt₂ leads to an abrupt halt in polymerization and low yields, possibly due to deactivation of the catalyst by the proposed CTA.

The same observation can be done for the BOMg as CTA, where PDI has increased twice compared to run 9 and the number of chains of polyethylene is 11500 times lower for the polymerization with the CTA.

A comparison between both CTA cannot be made because the molar ratios of CTA used in both experiments are different.



6.4. Conclusions

The complex $(BIQ)FeCl_2$ has been prepared and characterized, and was found to be active for ethylene polymerization, 9300 g/mol·h·bar, at high pressure in the presence of MAO and MMAO. Significant yields of polyethylene and comprehensible kinetic profiles were obtained only at pressures of 20 bar for both obtained only at pressures of 20 bar or above. Polyethylene produced under these conditions features molecular weights of up to 107700 g/mol and a typical PDI of 1,9. The presence of TMA as an impurity in the activator solution does not affect the rate of polymerization, as similar kinetics were observed when using MAO and MMAO. Attempts to pursue catalyzed chain-transfer polymerization by addition of a potential chain transfer agent, diethylzinc or butyloctylmagnesium, have a deactivating effect on the polymerization system.

6.5. Future work

To help to determine the cause of the deactivating effect of diethylzinc addition to the polymerization system, interaction between the pre-catalyst, $(BIQ)FeCl_2$, and $ZnEt_2$ may be studied by NMR and infrared spectroscopy. A change in the polymerization procedure using the same components may also delay deactivation, allowing a greater yield of polyethylene to be obtained, from which molecular weight data may allow the observation of any chain transfer.

To know which chain-transfer agent, $ZnEt_2$ or BOMg, is better for this catalyzed chain transfer polymerization a polymerization with the same operational conditions and molar ratios between cocatalyst/catalyst and CTA/catalyst should be done. If polyethylene production is higher for one of both and also with lower M_n , it means that chain exchange will occur more for this CTA and would be more suitable as CTA for the CCTP.



7. Ethylene polymerization with [(BPI)ZrBn₂] complex

7.1. Theoretical introduction

The development of group 4 metallocenes and MAO by made polymerization catalyst industrially practical. This fact has driven many researchers to investigate highly post-metallocene catalyst.

Makio et al. reported a series of dichlorozirconiumbis(phenoxyimine) complexes ([Phoxim₂ZrCl₂], Figure 18) which were active as ethylene polymerization catalysts in the presence of MAO [16]. The greatest activity was reported where R¹ = Ph, R² = *t*-Bu and R³ = H, and found to be 20 times higher than that of a zirconium metallocene catalyst with MAO.

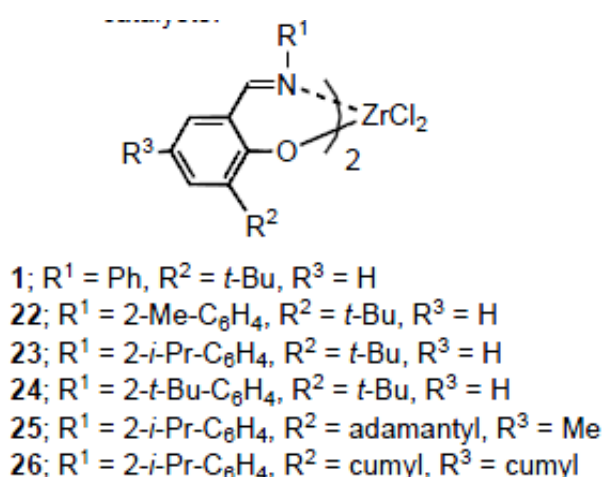


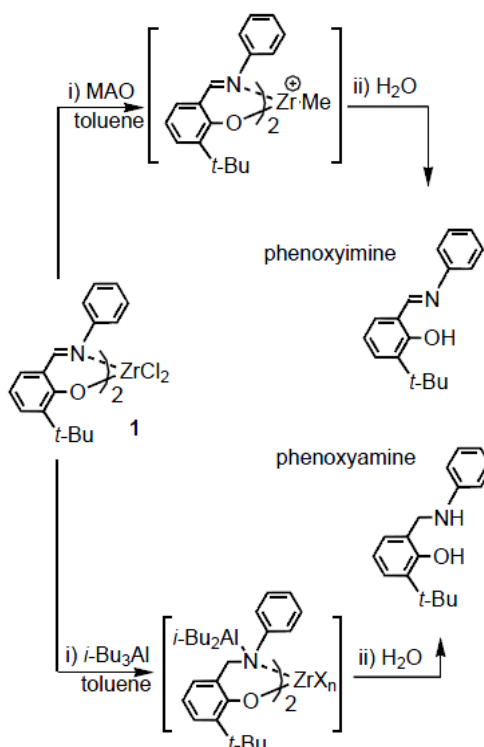
Figure 18: Zr FI catalysts by Makio et al. [16]

When [Phoxim₂ZrCl₂] complexes were activated by a combination of trityl tetrakis-(perfluorophenyl)borate [Ph₃CB(C₆F₅)₄] and trialkyl aluminium in addition to MAO for ethylene polymerization, high molecular weight polyethylene was obtained. The possible reactions between the [Phoxim₂ZrCl₂] catalysts and alkylaluminiums were studied by Makio and coworkers [16] and are summarized in Scheme 7.

Arriola and coworkers [10] reported the copolymerization of ethylene and octene using a mixture of a zirconium bis(phenoxyimine) catalyst and a hafnium pyridylamide catalyst with ZnEt₂ as a chain shuttling agent (CSA). Copolymers with lower molecular weight were obtained when CSA was used in the copolymerization.



For this study a zirconium bis(phenoxyimine) complex was prepared according to a literature procedure, by reaction of the 2 equivalents of the phenol-imine proligand with tetrabenzylzirconium. Polymerization studies were carried out using trityl tetra(pentafluorophenyl)borate or MAO as activators, and ZnEt_2 as a CTA.



Scheme 7: Possible reactions between $[\text{Phoxim}_2\text{ZrCl}_2]$ catalysts and alkylaluminiums: activation or ligand decomposition [16]

7.2. Experimental section

7.2.1. General considerations

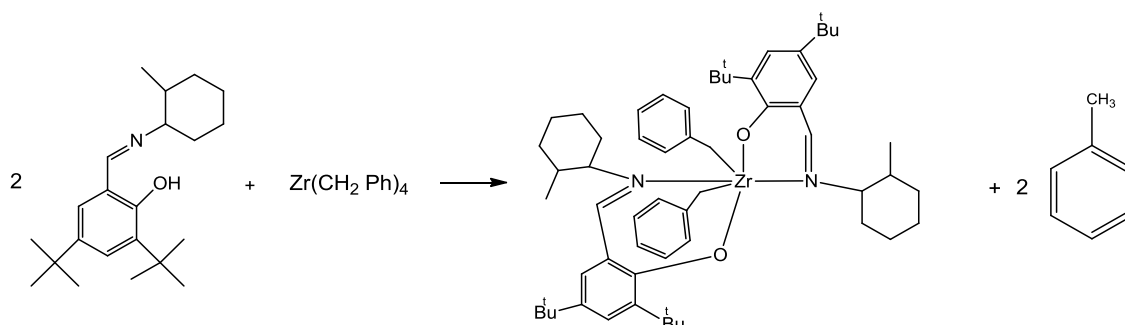
All manipulations of air- and moisture-sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques. Dried toluene was extracted from a MBraun-SPS 800 fountain. Isopar E (b.p. = 116°C) was purchased from. 30% wt MAO in toluene and 15% wt ZnEt_2 in toluene (1,1M) were purchased from Aldrich. 2,4-di-*tert*-butyl-6-((2-methylcyclohexylamino)methyl)phenol was stored inside the glove box in LCPP. All other chemicals were purchased from Aldrich or Acros Chemicals. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II 250 spectrometer operating at 250 MHz. Molecular weights of PE were determined by size exclusion chromatography (SEC) using a Waters Alliance GPCV 2000 instrument.



7.2.2. Synthesis of dibenzylzirconium bis(phenoxyimine), (BPI)ZrBn₂

Synthesis of the (BPI)ZrBn₂ complex (*Scheme 8*) was achieved with 2,4-di-tertbutyl-6-((2-methylcyclohexylamino)methyl)phenol ligand, synthesized by Dr. Paredes at LCPP.

To a Schlenk flask the ligand was introduced (103,8mg; 315μmol) with 10ml of Isopar E. A solution of tetrabenzyl zirconium (71,8mg; 157,5μmol) with 50ml of Isopar E was prepared in a separate Schlenk flask. The tetrabenzyl zirconium solution was slowly transferred with a 16-gauge metallic cannule to the ligand Schlenk flask and then the whole dark yellow solution was transferred to the 150ml Schlenk. The mixture was stirred for one hour, then 40ml of Isopar E were added and the solution was stirred for two more hours. An orange (BPI)ZrBn₂ solution in Isopar E was obtained (1,575mM) which was stored in the freezer.



Scheme 8: Synthesis of (BPI)ZrBn₂

The (BPI)ZrBn₂ complex solution was stored in the at -18°C to prevent thermal or light-activated decomposition. Before use in polymerizations, the solution was allowed to warm to room temperature.

7.2.3. Ethylene polymerization

All the polymerizations were performed in dried Isopar E as solvent and trityl tetra(pentafluorophenyl)borate, (C₆H₅)₃C⁺(C₆F₅)₄B⁻, used as an activator for the precatalyst, (BPI)ZrBn₂. MAO was used as a scavenger agent, to remove protic impurities, as described in the literature [17].

A 500ml glass reactor (*Figure 16*) was used to run the polymerizations. Argon supply and ethylene ballast were connected to the reactor.

Solutions of (C₆H₅)₃C⁺(C₆F₅)₄B⁻ and MAO in Isopar E, were added to the reactor under an argon atmosphere. The reactor was heated to the required polymerization temperature, the argon atmosphere was replaced with ethylene atmosphere, whereupon a solution of (BPI)ZrBn₂ (1,58 mM in Isopar) was added by the airlock (*Figure 16*) under ethylene



atmosphere. Ethylene pressure was increased at the desired pressure for polymerization. The reaction mixture was then stirred for the required polymerization time.

To terminate the polymerization, the reaction mixture was cooled and excess ethanol was added. The polymer obtained was washed with acidic ethanol, then ethanol, then filtered and dried. Results of all polymerizations are shown in *section 7.2.5*.

7.2.4. Polymerization using a chain-transfer agent (CTA)

In a 500ml Schlenk a solution of $(\text{C}_6\text{H}_5)_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$ and ZnEt_2 was prepared in dried Isopar E and immediately was introduced into the reactor.

The reactor was then heated to the required temperature with stirring at 600 rpm. An ethylene atmosphere was then introduced to the required pressure. The polymerization was then started by introduction of a $(\text{BIP})\text{ZrBn}_2$ solution.

After the required time or ethylene consumption, ethanol was added to quench zinc alkyl species and the polymer recovered as described in *section 6.2.4*.

7.2.5. Results and discussion

The complex $(\text{BIP})\text{ZrBn}_2$ solution in Isopar E was dried and characterized. The ^1H NMR spectrum of $(\text{BIP})\text{ZrBn}_2$ is shown in *Figure 19*. The fourteen aromatics protons appear at 7ppm. And from 1,64 to 1,31ppm appear the 68 non-aromatic protons.

The mechanism for the ethylene polymerization expected from the $(\text{BIP})\text{ZrBn}_2$ and the $(\text{C}_6\text{H}_5)_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$ catalytic system is shown in *Scheme 9*. This mechanism shows how the $(\text{C}_6\text{H}_5)_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$ activates the zirconium complex to act as a catalyst for the polymerization leaving a vacant site in the zirconium complex to allow ethylene's coordination and insertion.

Experiment 13 (Table 4) which was run with the objective to know if zirconium complex, acting as catalyst, and $(\text{C}_6\text{H}_5)_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$, acting as cocatalyst, are suitable to polymerize ethylene as expected (*Scheme 9*). This system is not active for ethylene polymerization because no activity is shown. The mechanism proposed, *Scheme 9*, is not valid for ethylene polymerization.



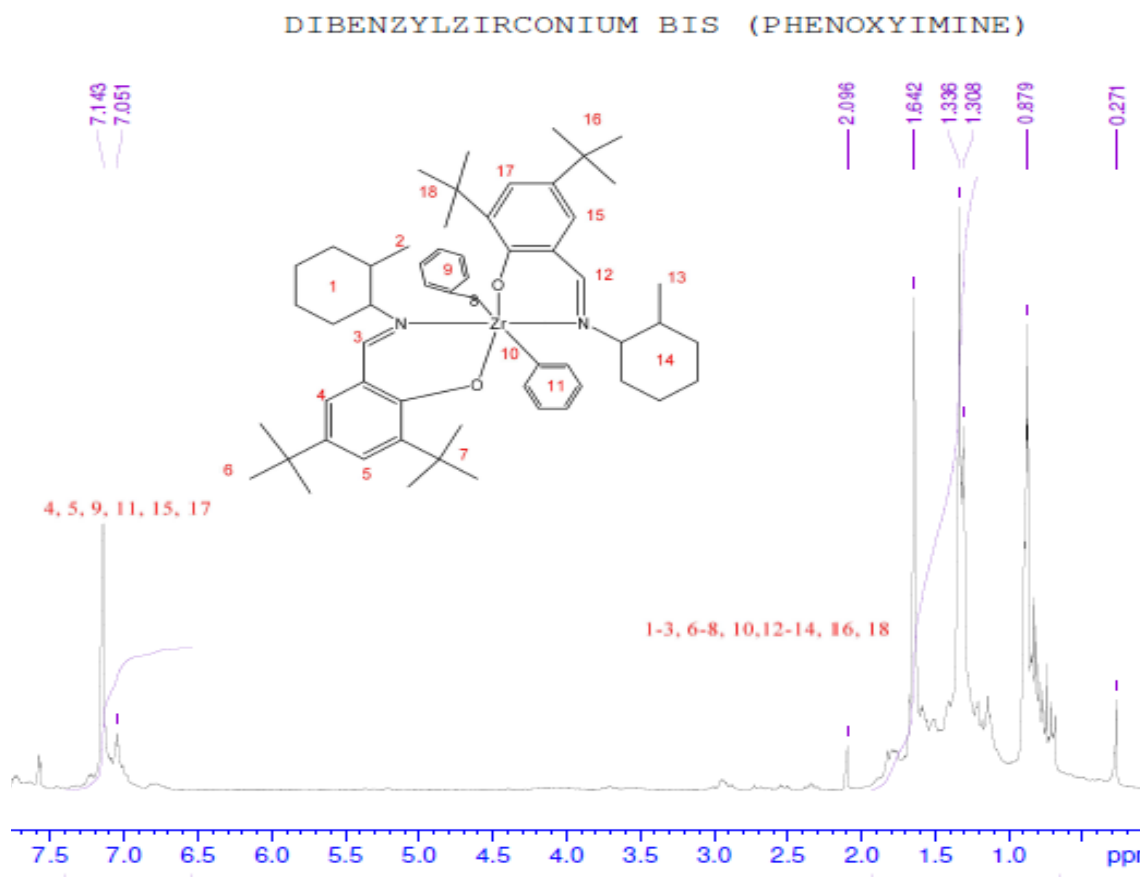


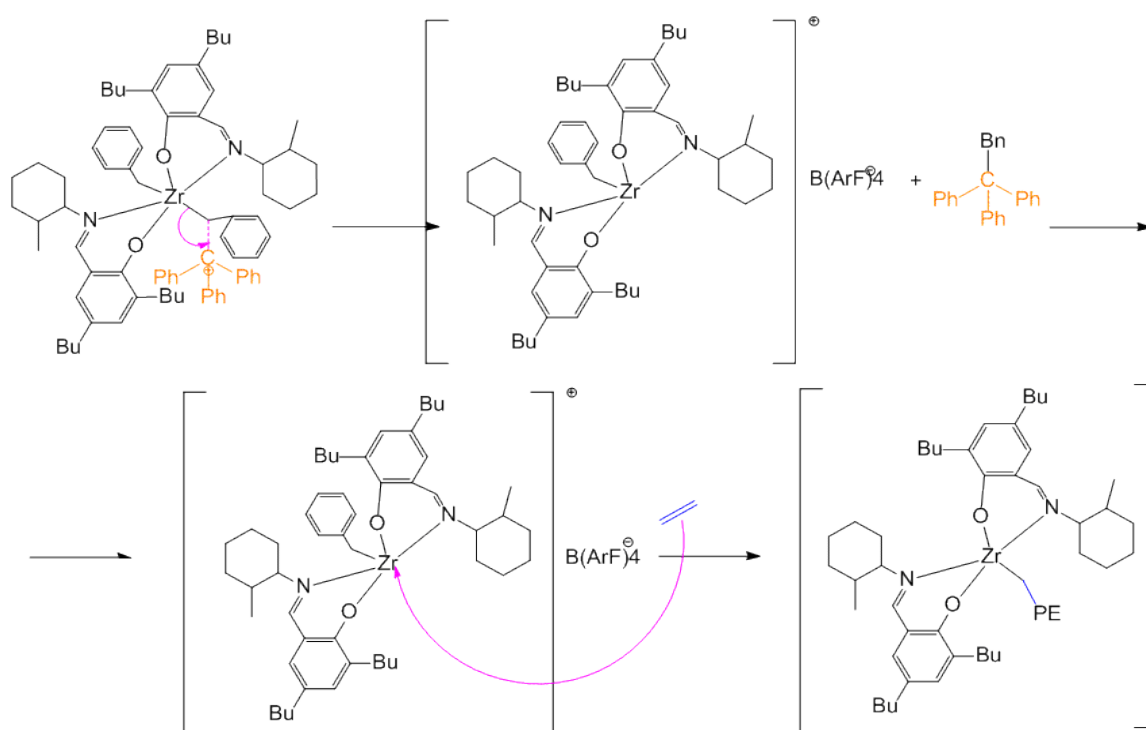
Figure 19: (BPI)ZrBn₂ ¹H NMR spectrum at room temperature in C₆D₆

When MAO in excess is added, experiments 14 and 15 (Table 4), the activity for this polymerization system observed was $8,4 \cdot 10^6$ and $9,9 \cdot 10^6$ g/mol·h·bar, 2,8g and 1,04g of polyethylene were produced for runs 14 and 15 respectively. Activities were calculated as if they have happened in twenty seconds. The polyethylene was obtained with M_n of 21312 and 75173 g/mol respectively and with a moderate PDI of 1,8 and 3,2 respectively. As there are more polyethylene chains for run 14 ($1,31 \cdot 10^{-4}$ mol PE) rather than for experiment 15 ($1,38 \cdot 10^{-5}$) and a higher PDI rate for the latter it suggests that higher ratio of MAO/(BPI)ZrBn₂ is making the initiation of the polymerization quicker for this system and it is shown with the higher amount of polyethylene obtained in experiment 14.



The difference in the activity upon the addition of MAO in the system, as a second activator, suggests that the addition of a methyl group is required to initiate the polymerization because the benzyl group doesn't insert effectively (*Scheme 9*).

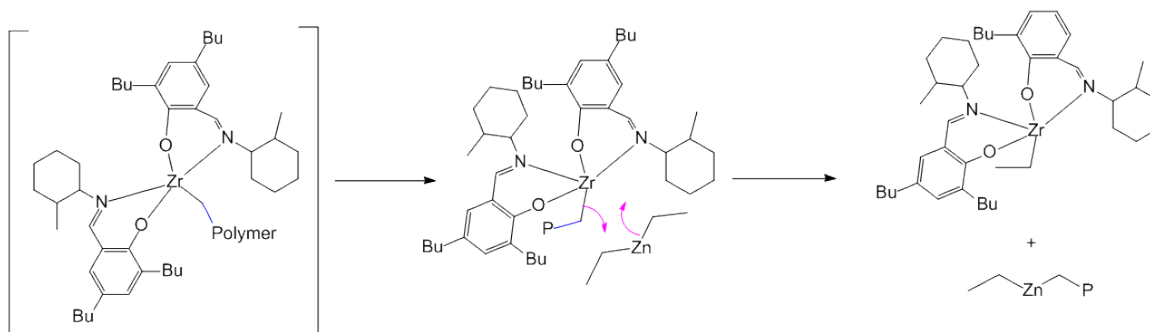
The $(C_6H_5)_3C^+(C_6F_5)_4B^-$ is a very sensitive complex. One of the reasons that polymerizations were stopped could be because tetra(pentafluorophenyl)borate was reacting with MAO in the case of runs 14 and 15 or with $ZnEt_2$ in run 16 to make some metallic complex. If this has happened, the complex $(BPI)ZrBn_2$ was not forming the cationic complex, look at *Scheme 9*, and ethylene was not able to be coordinated and neither inserted.



Scheme 9: Ethylene polymerization with $(BPI)ZrBn_2$ and $(C_6H_5)_3C^+(C_6F_5)_4B^-$



The experiment 16 was run using ZnEt_2 as a possible CTA. The reaction expected is showed in *Scheme 10*.



Scheme 10: Ethylene polymerization with (BPI)ZrBn₂, (C₆H₅)₃C⁺(C₆F₅)₄B⁻ and ZnEt₂ as CTA

When a CTA is introduced to the system of (BPI)ZrBn₂ catalyst and borate cocatalyst, experiment 16 (Table 4), no polymerization activity was observed and ZnEt₂ failed to activate the catalyst system. This could probably mean that some other aggregates which were more stable than the expected (*Scheme 10*) were created and polymerization of ethylene wasn't achieved.



Experiment	P (bar)	T (°C)	(BPI)ZrBn ₂ (μM)	Mol (C ₆ H ₅) ₃ C ⁺ (C ₆ F ₅) ₄ B ⁻ / (BPI)ZrBn ₂	Mol MAO/ (BPI)ZrBn ₂	Mol ZnEt ₂ / (BPI)ZrBn ₂	Yield (g)	Activity (g/mol*h*bar)	M _n (g/mol)	PDI	Mol PE obtained	Mol PE obtained / mol (BPI)ZrBn ₂
13	3,8	112	52,5	0,1	-	-	0	-	-	-	-	-
14	3,8	113	52,5	0,1	1916	-	2,8	8,40E+06	21312	1,8	1,31E- 04	8,3
15	4,2	110	15	1	33	-	1,04	9,90E+06	75173	3,2	1,38E- 05	3,1
16	4,2	116	30	1	-	87	0	-	-	-	-	-

Table 4: Ethylene polymerization in glass reactor

7.3. Conclusions

The polymerization operational conditions for the system $(\text{BPI})\text{ZrBn}_2/(\text{C}_6\text{H}_5)_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-/\text{MAO}$ were not achieved at all because the polymerization was stopped after a few seconds. Molecular weight control of the polyethylene by CCTP with ZnEt_2 as a CTA wasn't achieved and functionalization of the polyethylene was not done because polymerization wasn't achieved.

7.4. Future work

In order to achieve polymerization activity using the catalyst system $(\text{BPI})\text{ZrBn}_2$ with $(\text{C}_6\text{H}_5)_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$, the polymerization procedure may require adaptation, specifically the inclusion of an 'activation period' prior to introduction of ethylene or any chain-transfer agents. Investigation into the effects of the identity of the initiating alkyl group may help to achieve active catalyst systems. In addition, testing a range of potential chain-transfer agents for their compatibility with this system may allow access to polymers with tunable molecular weight and end-group functionality.



8. Acknowledgment

I want to express my most sincere thanks to Dr Ian German for all his teaching about organic and inorganic chemistry in the lab, his support at all times and for being such a good friend for all of this period. And also lots of thanks for correcting this report.

Thanks to the C2P2 lab, with Bernadette Charleux as the head, for giving me the opportunity to work inside a lab.

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Lots of thanks to all the people that work in the LCPP: Aurelie, Benoit, Bérèngère, Cédric, Céline, Gerome, Geoffroy, Jean-Pierre, Julian, Elena, Dr Ethiene, Estevan, Guilhem, Nathalie, Olivier, Pierre, Pierre-Yves, Dr Roger, Dr Vincent, Virginie.

Thanks to my family and my friends who have supported me throughout my university studies and made it possible for me to become a Chemical Engineer one day, without them this wouldn't be possible.



9. Bibliography

9.1. Articles, books and websites

- [1] <http://www.ides.com/info/generics/27/Polyethylene-PE> (consulted 13/07/11)
- [2] Andrew J. Peacock, Handbook of polyethylene: structures, properties, and applications, **2000** – Marcel Dekker
- [3] Cossee, P. J. Catal., **1964**, 3, 80-88
- [4] W. Kaminsky, Catalysis, **2000**, 46, 89-159
- [5] Jérôme Mazzolini, Edgar Espinosa, Franck d'Agosto and Christophe Boisson, Polym. Chem., **2010**, 1, 793-800
- [6] Helmut G. Alt, and Alexander Köppl, Chem. Rev., **2000**, 100, 1205-1221
- [7] L. Reconi, I. Camurati, and O. Sudmeijer, Top. Catal., **1999**, 7, 145-163
- [8] George J. P. Britovsek, Steven A. Cohen, Vernon C. Gibson, and Martin van Meurs, *J. Am. Chem. Soc.*, **2004**, 126 (34), 10701–10712
- [9] Vernon C. Gibson, Science, **2006**, 312, 703-704
- [10] Daniel J. Arriola, Edmund M. Carnahan, Phillip D. Hustad, Roger L. Kuhlman, Timothy T. Wenzel, Science, **2006**, 312, 714-719
- [11] George J. P. Britovsek, Vernon C. Gibson, Brian S. Kimberley, Peter J. Maddox, Stuart J. McTavish, Gregory A. Solan, Andrew J. P. White and David J. Williams, *Chem. Commun.*, **1998**, 849-850
- [12] George J. P. Britovsek, *Michael Bruce*, Vernon C. Gibson, Brian S. Kimberley, Peter J. Maddox, *Sergio Mastroianni*, Stuart J. McTavish,, Carl Redshaw, Gregory A. Solan, Staffan Strömberg, Andrew J. P. White and David J. Williams, *J. Am. Chem. Soc.*, **1999**, 8728-8740
- [13] Konstantin P. Bryliakov, Nina V. Semikolenova, Vladimir N. Zudin, Vladimir A. Zakharov, and Evgenii P. Talsi, Catalysis Communications 5, **2004**, 45-48
- [14] Shu Zhang, Wen-Hua Sun, Tianpengfei Xiao, and Xiang Hao, Organometallics, **2010**, 20, 1168-1173
- [15] Vincenzo Busico, Roberta Cipullo, Francesco Cutillo, Nic. Friederichs, Sara Ronca, and Bing Wang, *J. Am. Chem. Soc.*, **2003**, 125, 12402-12403
- [16] H. Makio, N. Kashiwa, and T. Fujita, Adv. Synth. Catal., **2002**, 344, 477-493
- [17] Phillip D. Hustad, Roger L. Kuhlman, Daniel J. Arriola, Edmund M. Carnahan, and Timothy T. Wenzel, Macromolecules, **2007**, 40, 7061-7064



9.2. Additional bibliography

- [18] <http://plasticpipe.org/pdf/chapter03.pdf> (consulted 13/07/11)
- [19] William D. Calister, Introducción a la ciencia e ingeniería de los materiales, 2007 – Reverté
- [20] <http://classes.uleth.ca/200701/chem4000a/Class%20Notes%20Web%20Pages/Olefin%20Polymerization/Olefin%20Polymerization.pdf> (consulted 13/07/11)
- [21] http://www.eurisotop.com/nmr_solvents (consulted march 2011)
- [22] Applied Catalysis A: General 222, **2001**, 47–61
- [23] R. Mülhaupt, Macromol. Chem. Phys. **2003**, 204, 289-327



10. Appendix

10.1. Infra Red Spectra

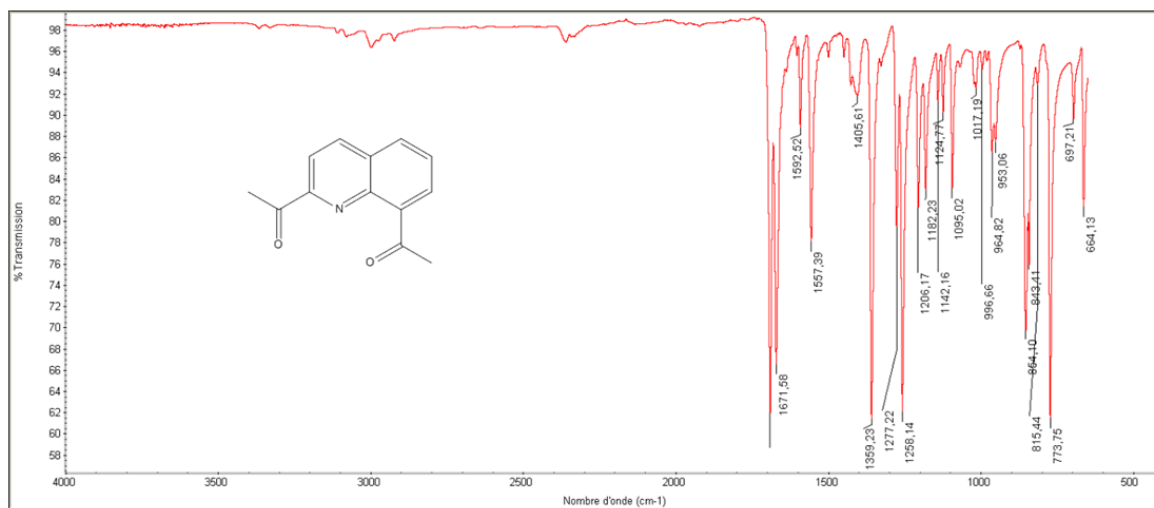


Figure 20: Quinoline IR spectrum

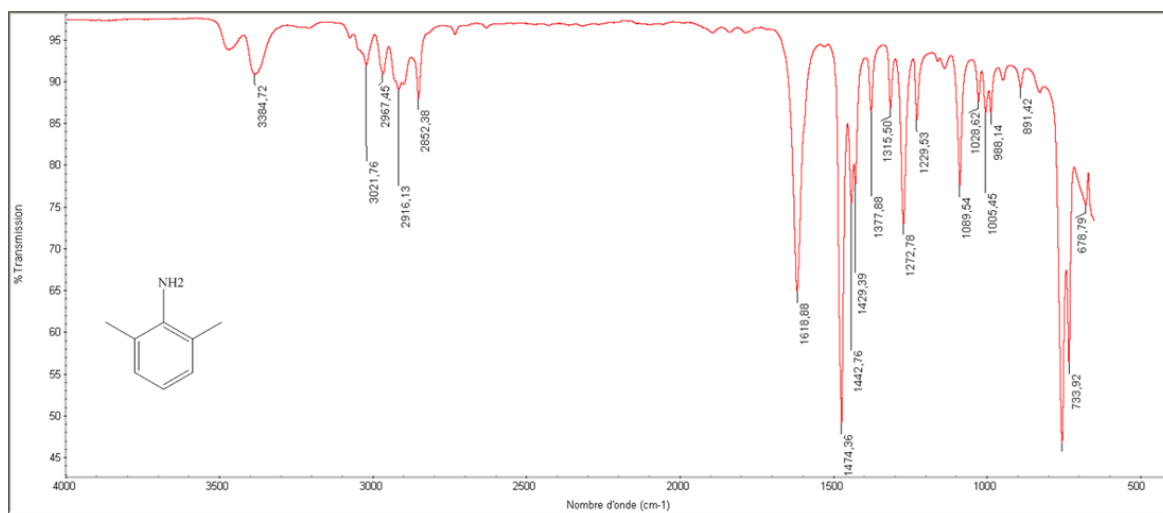


Figure 21: Aniline spectrum IR



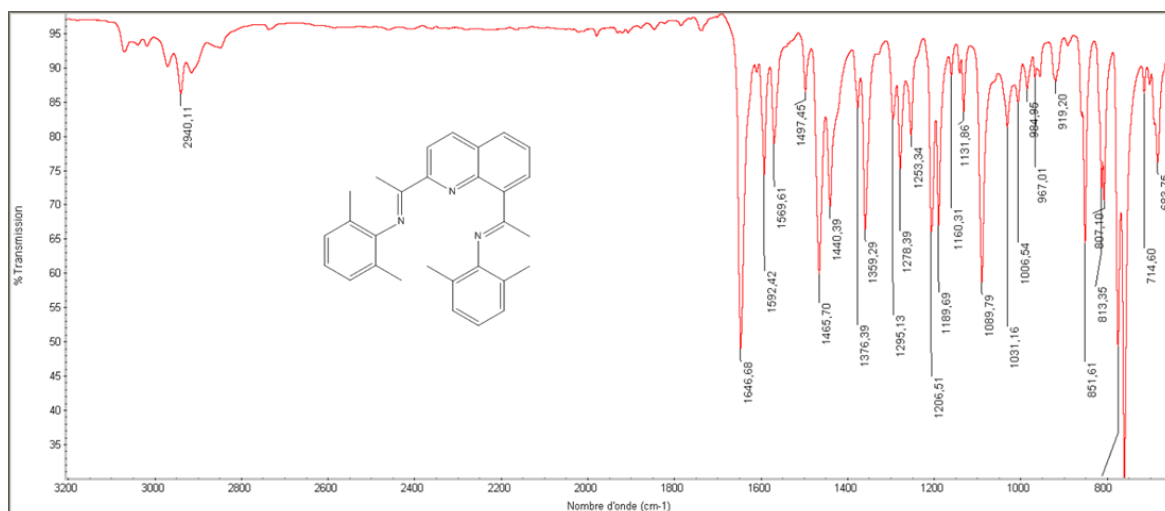
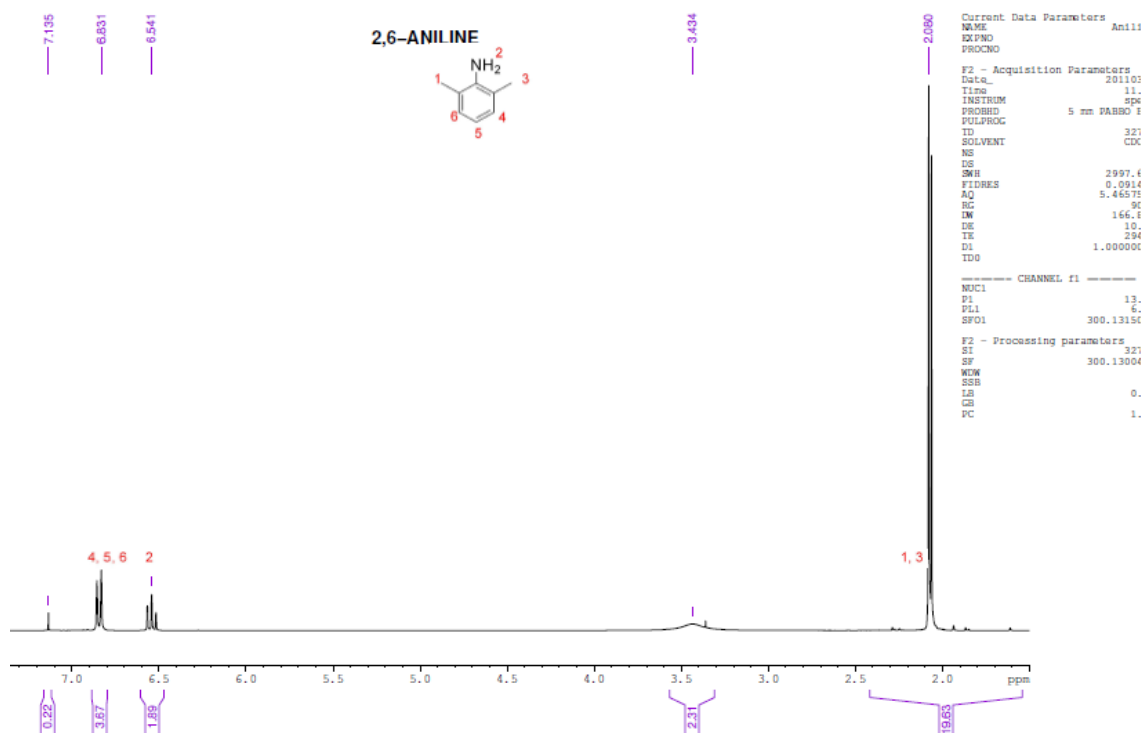


Figure 22: Ligand (BQI) IR spectrum

10.2. ^1H Nuclear Magnetic Resonance Spectra

Figure 23: 2,6-dimethylaniline ^1H NMR spectrum, solvent: CDCl_3 , room temperature

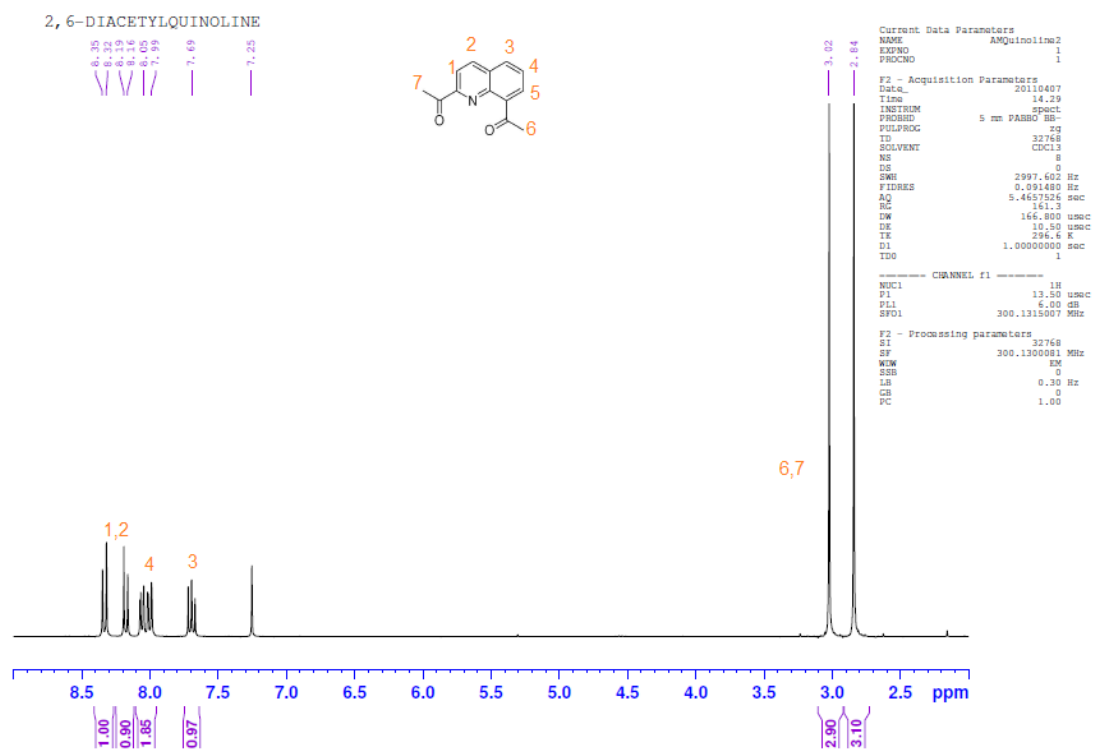


Figure 24: 2,6-diacetylquinoline ^1H NMR spectrum, solvent: CDCl_3 , room temperature

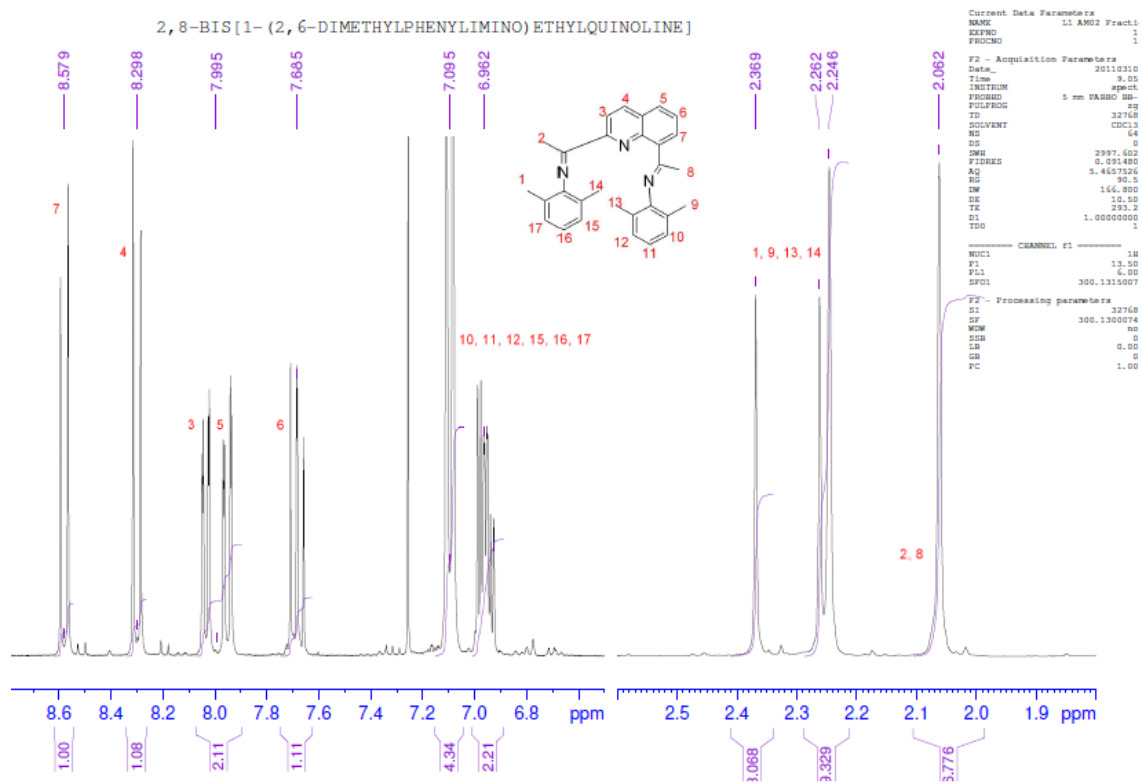


Figure 25: (BQI) ^1H NMR spectrum, solvent: CDCl_3 , room temperature



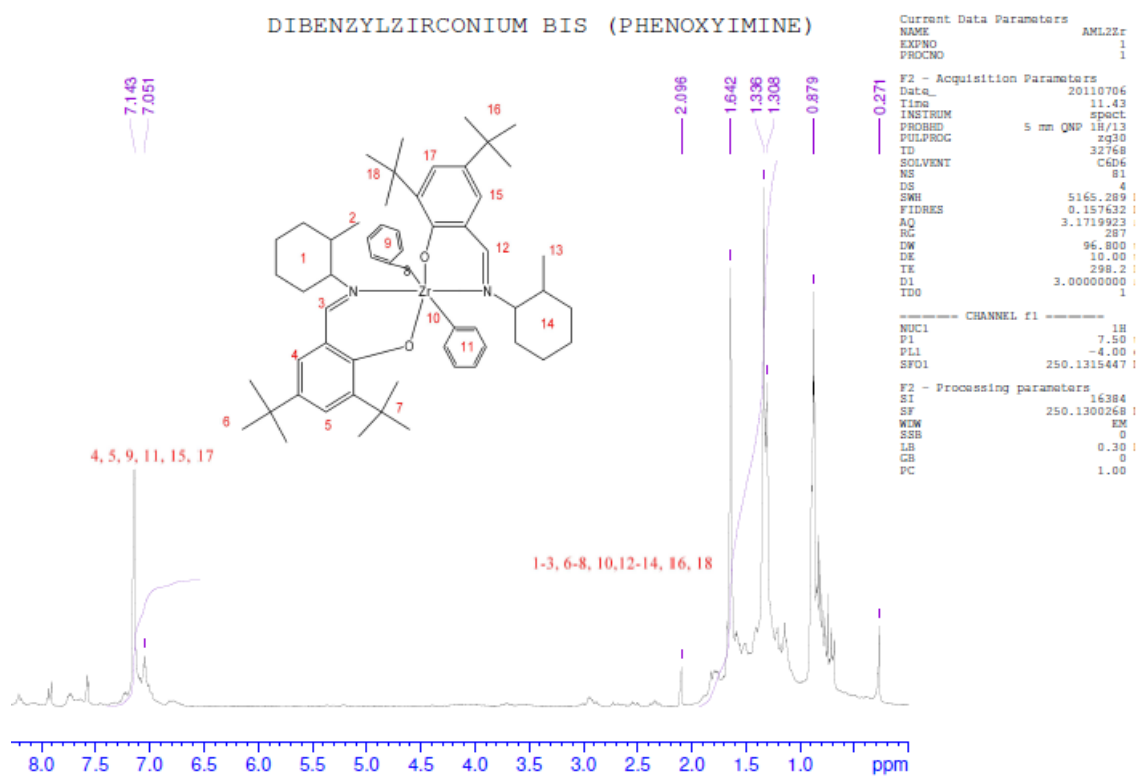


Figure 26: $(BPI)ZrBn_2$ 1H NMR spectrum, solvent: C_6D_6 , room temperature

10.3. Size Exclusion Chromatography



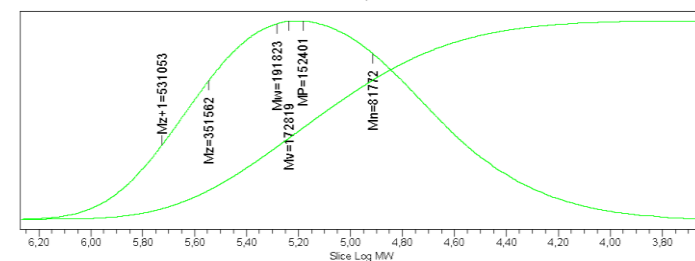
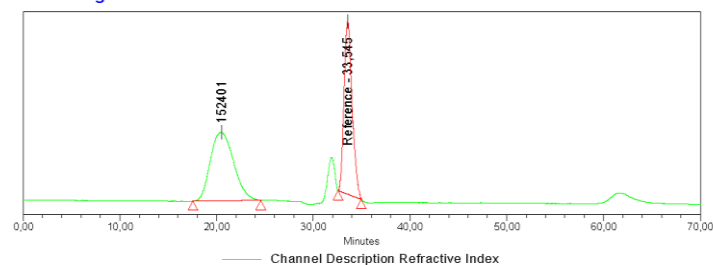


C2P2 - UMR5265

Analytical report High Temperature Size Exclusion Chromatography

Sample Name: AM11 Sample Type: Broad Unknown
 Vial: 9 Date Acquired: 21/05/2011 06:35:00
 Injection #: 1 Acq. Method Set:
 Injection Volume: 318,50 μ l Date Processed: 23/05/2011 10:53:28
 Run Time: 70 minutes Processing Method: CalibPSuniv

Chromatogram



Results

	RTime (min)	Mn	Mw	Mp	Ip	g'	K	alpha	[η]w (dl/g)	Intrinsic Viscosity	Area (μ V*sec)	% Area	Conc	g' LCB	g' SCB	lambda
1	20.5	81772	191823	152401	2.3		0.0005	0.7060		2.359	1276252	53.31				
2	33.5										1117824	46.69				



C2P2 - UMR5265

Results

	Linear alpha	Linear K (dl/g)
1		
2		

Viscosity Law Plot

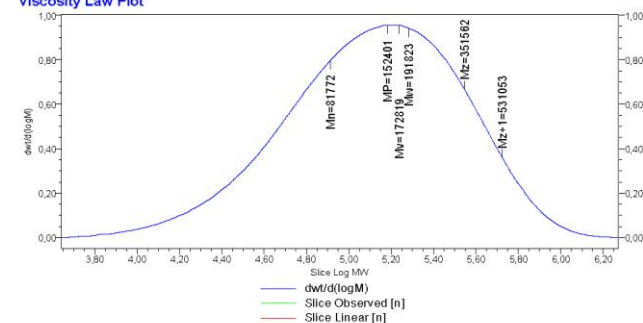
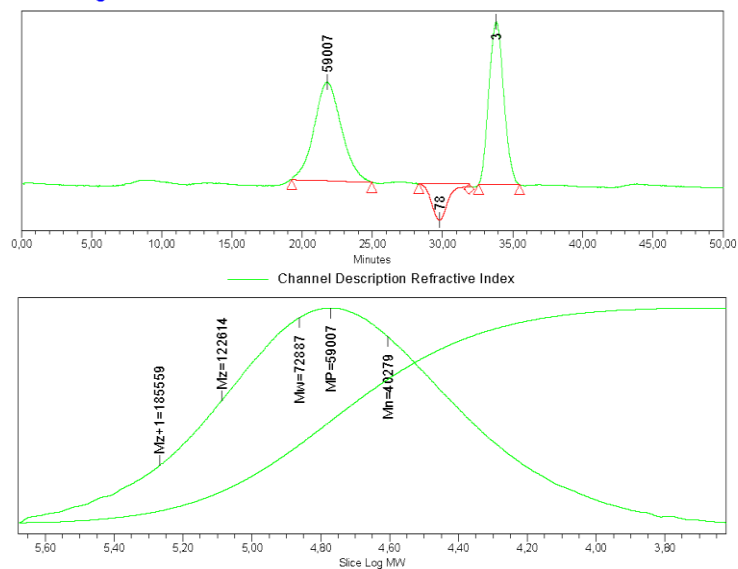


Figure 27: SEC data for run 2 (Table 1)

Analytical report
High Temperature Size Exclusion Chromatography

Sample Name: AM20 Sample Type: Broad Unknown
Vial: 14 Date Acquired: 28/06/2011 09:11:00
Injection #: 1 Acq. Method Set:
Injection Volume: 318,50 μ l Date Processed: 29/06/2011 18:13:43
Run Time: 70 minutes Processing Method: CalibPE

Chromatogram**Results**

	RT (min)	Mn	Mw	Mp	Ip	g'	K	alpha	[η] (d/g)	Intrinsic Viscosity	Area (μ V \cdot sec)	% Area	Conc	g' LCB	g' SCB	lambda	Linear alpha
1	21.8	40279	72887	59007	1.8						1254567	47.28					
2	29.8			78							277157	10.44					
3	33.8			3							1122010	42.28					

Report Method: SEC Individual Report

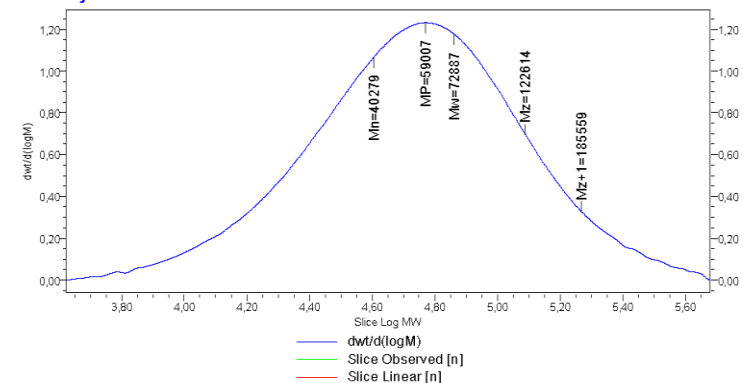
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29/06/2011

Page: 1 of 2

Results

	Linear K (d/g)
1	
2	
3	

Viscosity Law Plot

Report Method: SEC Individual Report

Printed 18.14.01

29/06/2011

Page: 2 of 2

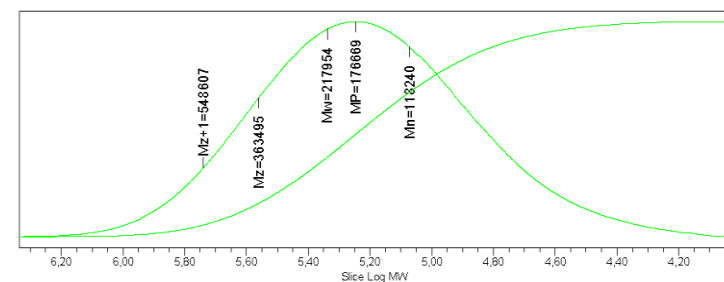
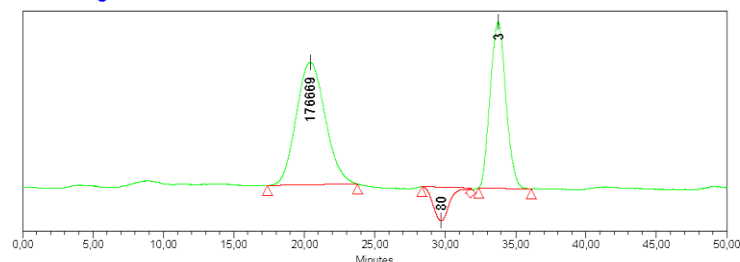
Figure 28: SEC data for run 3 (Table 1)



Analytical report High Temperature Size Exclusion Chromatography

Sample Name: AM22 Sample Type: Broad Unknown
 Vial: 16 Date Acquired: 28/06/2011 10:58:00
 Injection #: 1 Acq. Method Set: Date Processed: 29/06/2011 18:12:02
 Injection Volume: 318.50 µl Processing Method: CalibPE
 Run Time: 70 minutes

Chromatogram



Results

	RTTime (min)	Mh	Mv	Mp	Ip	g'	K	alpha	[η]w (dl/g)	Intrinsic Viscosity	Area (µV*sec)	% Area	Conc	g' LCB	g' SCB	lambda	Linear alpha
1	33.8			3							1211587	39.16					
2	29.7			80							244783	7.91					
3	20.4	118240	217954	176689	1.8						1637282	52.92					

Report Method: SEC Individual Report

Printed 18:12:28

29/06/2011

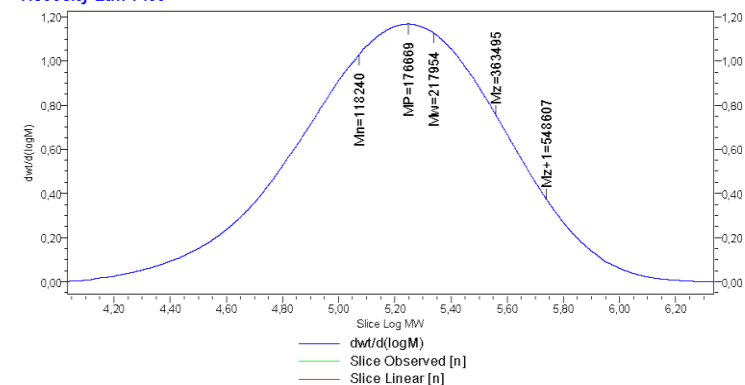
Page: 1 of 2



Results

	Linear K (dl/g)
1	
2	
3	

Viscosity Law Plot



Report Method: SEC Individual Report

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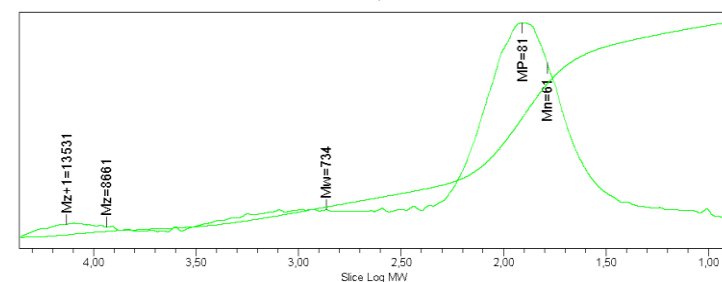
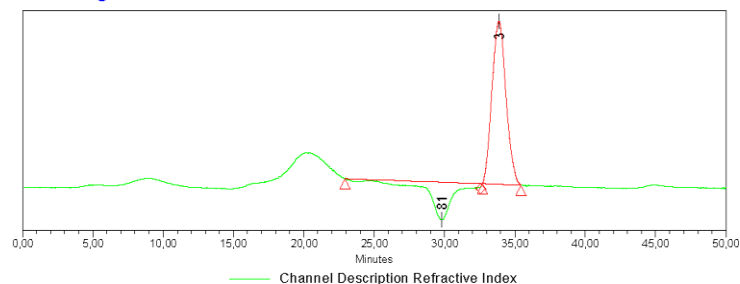
29/06/2011

Page: 2 of 2

Figure 29: SEC data for run 4 (Table 1)

Analytical report
High Temperature Size Exclusion Chromatography

Sample Name: AM18 Sample Type: Broad Unknown
Vial: 12 Date Acquired: 28/06/2011 07:25:00
Injection #: 1 Acq. Method Set:
Injection Volume: 318,50 µl Date Processed: 29/06/2011 18:33:04
Run Time: 70 minutes Processing Method: CalibPE

Chromatogram**Results**

	RTIME (min)	Mn	Mw	MP	IP	g'	K	alpha	[η] _{sp} /c (dl/g)	Intrinsic Viscosity	Area (µV*sec)	% Area	Conc	g' LCB	g' SCB	lambda	Linear alpha	Linear K (dl/g)
1	29,8	61	734	81	12,0						473080	28,83						
2	33,9			3							1167719	71,17						

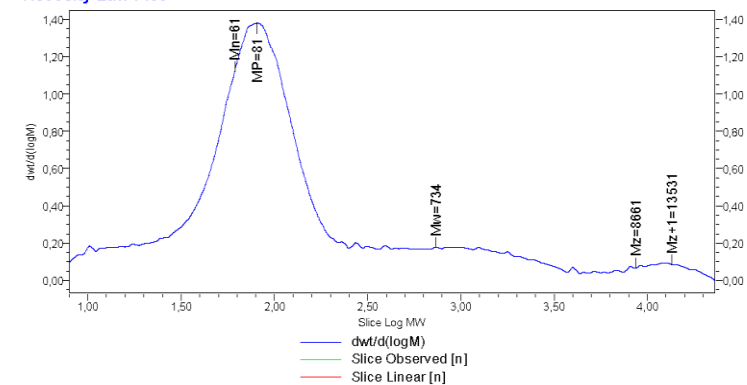
Viscosity Law Plot

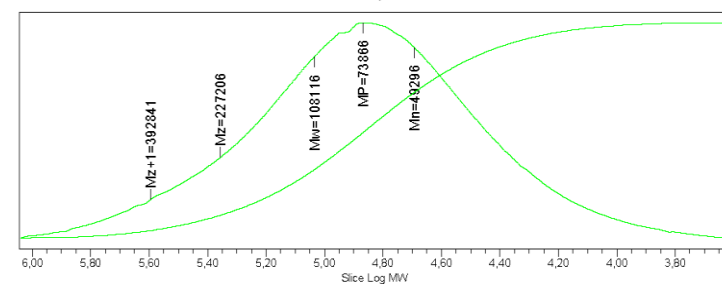
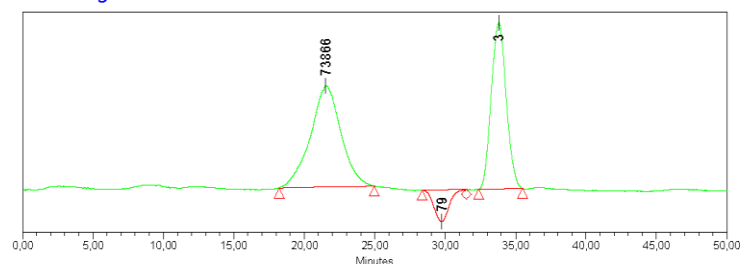
Figure 30: SEC data for run 5 (Table 2)



Analytical report High Temperature Size Exclusion Chromatography

Sample Name: AM19 Sample Type: Broad Unknown
 Vial: 13 Date Acquired: 28/06/2011 08:18:00
 Injection #: 1 Acq. Method Set:
 Injection Volume: 318,50 µl Date Processed: 29/06/2011 18:14:22
 Run Time: 70 minutes Processing Method: CalibPE

Chromatogram



Results

	RTTime (min)	Mn	Mw	Mp	Ip	g'	K	alpha	[η]w (dl/g)	Intrinsic Viscosity	Area (µV*sec)	% Area	Conc	g' LCB	g' SCB	lambda	Linear alpha
1	21,5	49296	108116	73866	2,2						1446940	51,26					
2	29,6			79							216346	7,67					
3	33,8			3							1159227	41,07					

Report Method: SEC Individual Report

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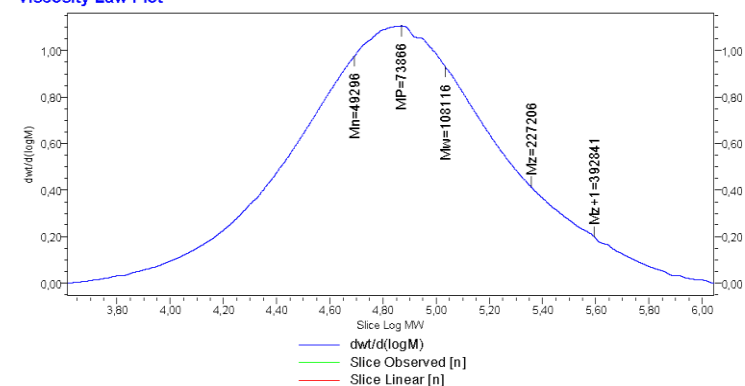
Page: 1 of 2



Results

	Linear K (dl/g)
1	
2	
3	

Viscosity Law Plot



Report Method: SEC Individual Report

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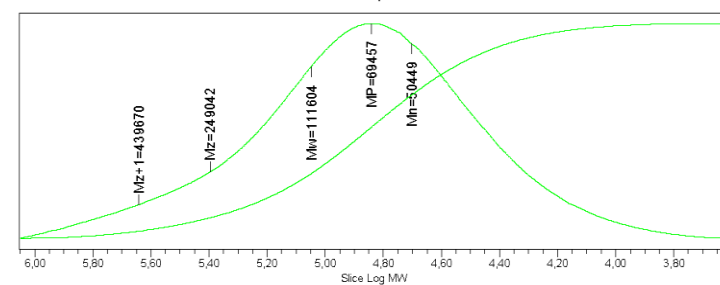
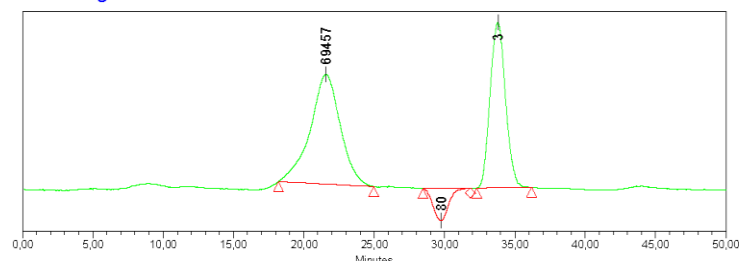
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Page: 2 of 2

Figure 31: SEC data for run 6 (Table 2)

Analytical report
High Temperature Size Exclusion Chromatography

Sample Name: AM21 Sample Type: Broad Unknown
Vial: 15 Date Acquired: 28/06/2011 10:05:00
Injection #: 1 Acq. Method Set:
Injection Volume: 318,50 µl Date Processed: 29/06/2011 18:13:01
Run Time: 70 minutes Processing Method: CalibPE

Chromatogram**Results**

	RTime (min)	Mn	Mw	Mp	Ip	g'	K	alpha	[η]w (dl/g)	Intrinsic Viscosity (µlV*sec)	Area (µV*sec)	% Area	Conc	g' LCB	g' SCB	lambda	Linear alpha
1	21,6	50449	111604	69457	2,2						1563454	52,31					
2	29,7			80							227885	7,62					
3	33,8			3							1197662	40,07					

Report Method: SEC Individual Report

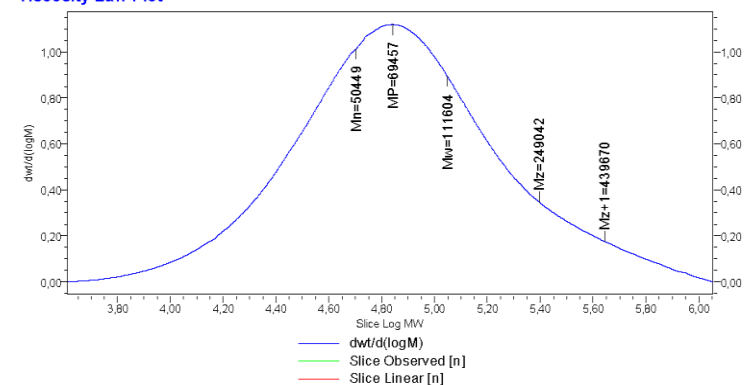
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Page: 1 of 2

Results

	Linear K (dl/g)
1	
2	
3	

Viscosity Law Plot

Report Method: SEC Individual Report

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Page: 2 of 2

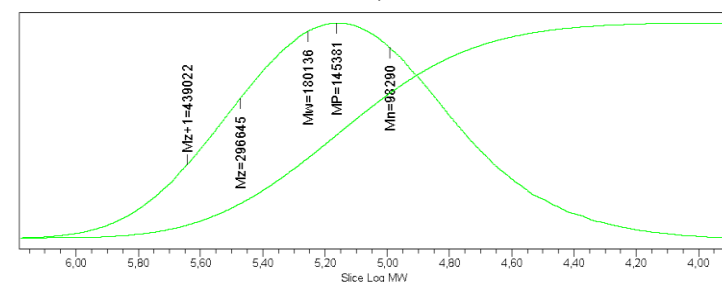
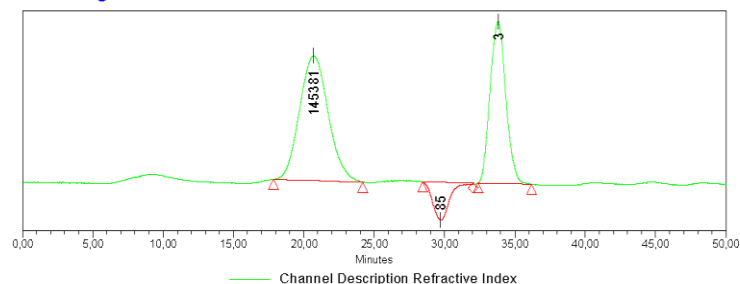
Figure 32: SEC data for run 7 (Table 2)



Analytical report High Temperature Size Exclusion Chromatography

Sample Name: AM23 Sample Type: Broad Unknown
 Vial: 17 Date Acquired: 28/06/2011 11:51:00
 Injection #: 1 Acq. Method Set:
 Injection Volume: 318.50 µl Date Processed: 29/06/2011 18:11:14
 Run Time: 70 minutes Processing Method: CalibPE

Chromatogram



Results

	RTime (min)	Mn	Mw	MP	Ip	g'	K	alpha	[η] ₀ (dl/g)	Intrinsic Viscosity	Area (µV*sec)	% Area	Conc	g' LCB	g' SCB	lambda	Linear alpha
1	20.7	98290	180136	145381	1.8						1595517	53.09					
2	29.7			85							266953	8.88					
3	33.8			3							1142776	38.03					

Report Method: SEC Individual Report

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29/06/2011

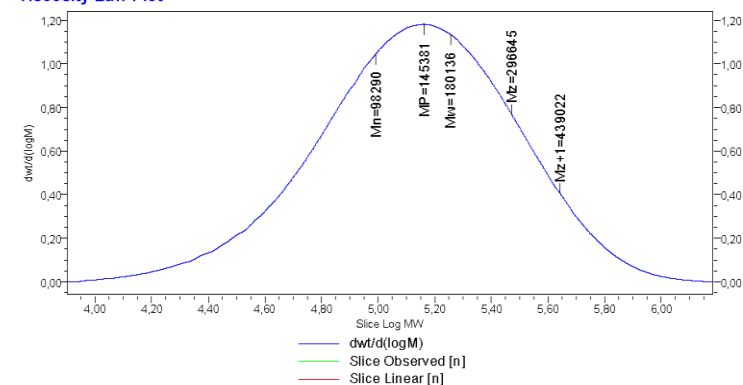
Page: 1 of 2



Results

	Linear K (dl/g)
1	
2	
3	

Viscosity Law Plot



Report Method: SEC Individual Report

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29/06/2011

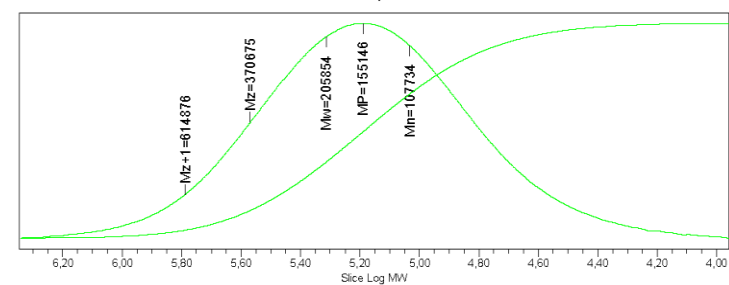
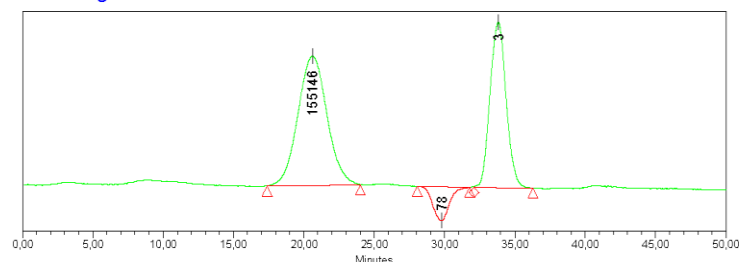
Page: 2 of 2

Figure 33: SEC data for run 8 (Table 2)

Analytical report
High Temperature Size Exclusion Chromatography

Sample Name: AM24
Vial: 18
Injection #: 1
Injection Volume: 318,50 μ l
Run Time: 70 minutes

Sample Type: Broad Unknown
Date Acquired: 28/06/2011 12:45:00
Acq. Method Set:
Date Processed: 29/06/2011 18:09:30
Processing Method: CalibPE

Chromatogram**Results**

	RTTime (min)	Mh	Mw	Mp	Ip	g'	K	alpha	[η] _w (dl/g)	Intrinsic Viscosity (μ V ² /sec)	Area (μ V ² /sec)	% Area	Conc	g' LCB	g' SCB	lambda	Linear alpha
1	20,6	107734	205854	155146	1,9						1786552	54,07					
2	29,8			78							254816	7,71					
3	33,8			3							1262693	38,22					

Report Method: SEC Individual Report

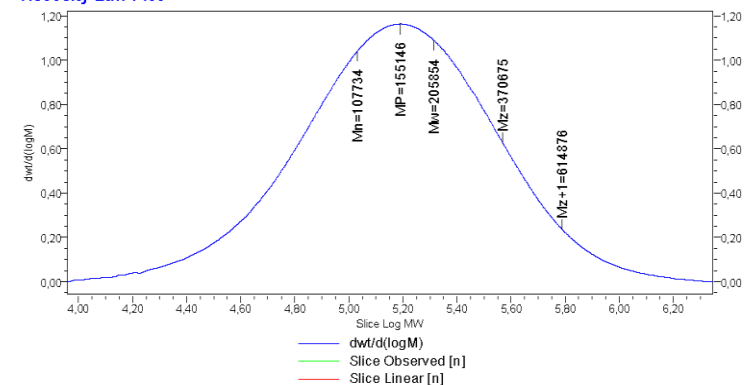
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29/06/2011

Page: 1 of 2

Results

	Linear K (dl/g)
1	
2	
3	

Viscosity Law Plot

Report Method: SEC Individual Report

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29/06/2011

Page: 2 of 2

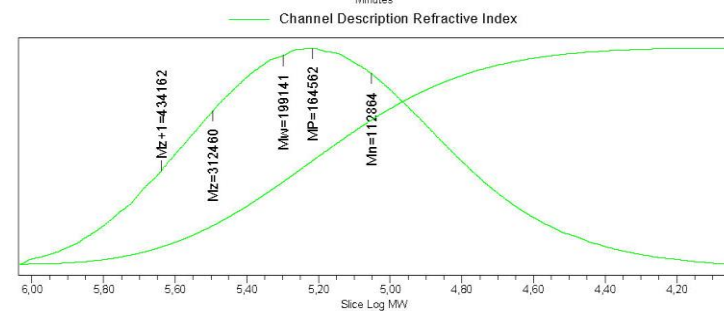
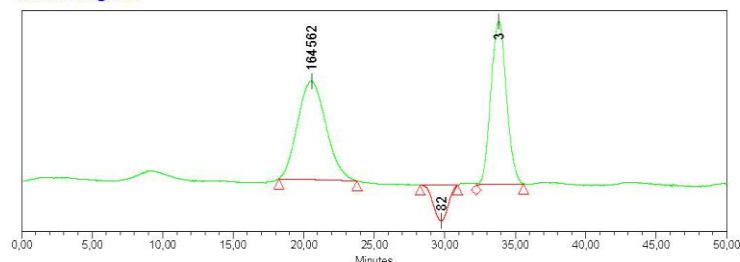
Figure 34: SEC data for run 9 (Table 2)



Analytical report High Temperature Size Exclusion Chromatography

Sample Name: AM25 Sample Type: Broad Unknown
 Vial: 19 Date Acquired: 28/06/2011 13:38:00
 Injection #: 1 Acq. Method Set:
 Injection Volume: 318,50 ul Date Processed: 29/06/2011 18:07:21
 Run Time: 70 minutes Processing Method: CalibPE

Chromatogram



Results

	RTTime (min)	Mn	Mw	Mp	Ip	g'	K	alpha	[η]w (dl/g)	Intrinsic Viscosity (μV*sec)	Area (μV*sec)	% Area	Conc	g' LCB	g' SCB	lambda	Linear alpha
1	20,6	112864	199141	164562	1,8						1137139	47,77					
2	29,8			82							210049	8,82					
3	33,8			3							1033192	43,40					

Report Method: SEC Individual Report

Printed 18/08/06

29/06/2011

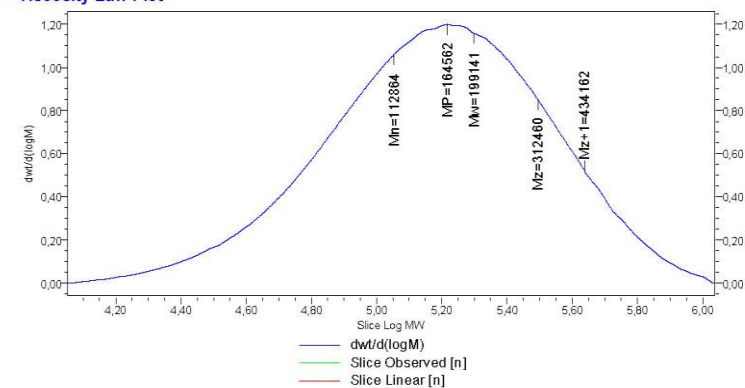
Page: 1 of 2



Results

	Linear K (dl/g)
1	
2	
3	

Viscosity Law Plot



Report Method: SEC Individual Report

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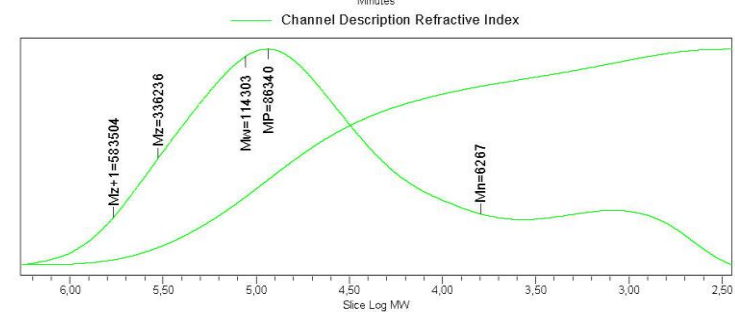
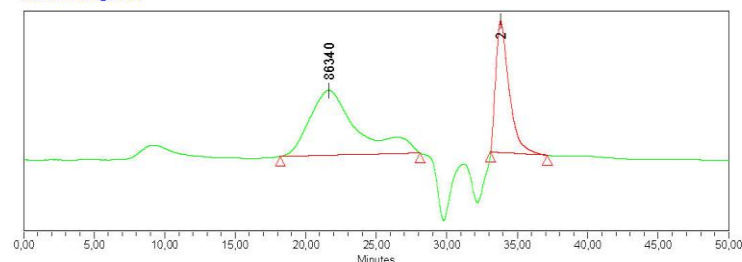
29/06/2011

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Figure 35: SEC data for run 10 (Table 2)

Analytical report
High Temperature Size Exclusion Chromatography

Sample Name: AM29 Sample Type: Broad Unknown
Vial: 18 Date Acquired: 25/08/2011 09:59:00
Injection #: 1 Acq. Method Set:
Injection Volume: 318,50 μ l Date Processed: 31/08/2011 10:28:31
Run Time: 70 minutes Processing Method: CalibPE

Chromatogram**Results**

	RTTime (min)	Mn	Mw	Mp	Ip	g	K	alpha	[η]w (dl/g)	Intrinsic Viscosity	Area (μ V \cdot s)	Conc
1	33.8			2							829406	
2	21.7	6267	114303	86340	18.2						1459029	

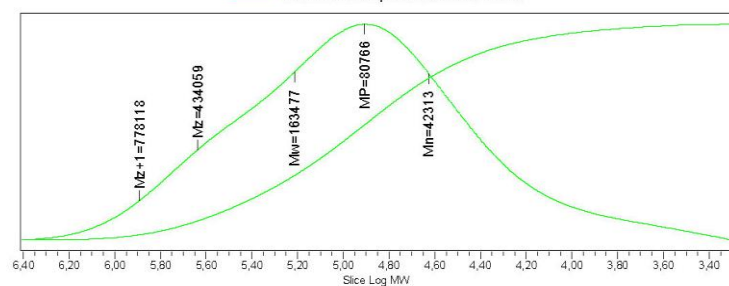
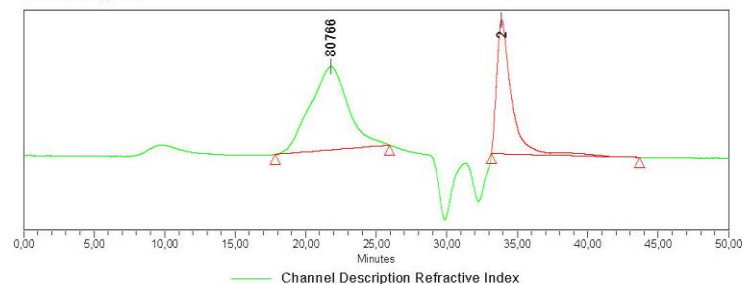
Figure 36: SEC data for run 11 (Table 3)



Analytical report High Temperature Size Exclusion Chromatography

Sample Name: AM30 Sample Type: Broad Unknown
 Vial: 19 Date Acquired: 25/08/2011 10:53:00
 Injection #: 1 Acq. Method Set:
 Injection Volume: 318,50 µl Date Processed: 31/08/2011 10:30:01
 Run Time: 70 minutes Processing Method: CalibPE

Chromatogram



Results

	RTime (min)	Mn	Mw	Mp	Ip	g'	K	alpha	[η]w (dl/g)	Intrinsic Viscosity	Area (µV*sec)	Conc
1	33,9			2							921464	
2	21,8	42313	163477	80766	3,9						1447733	

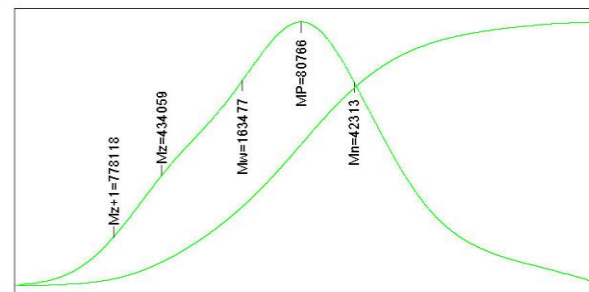
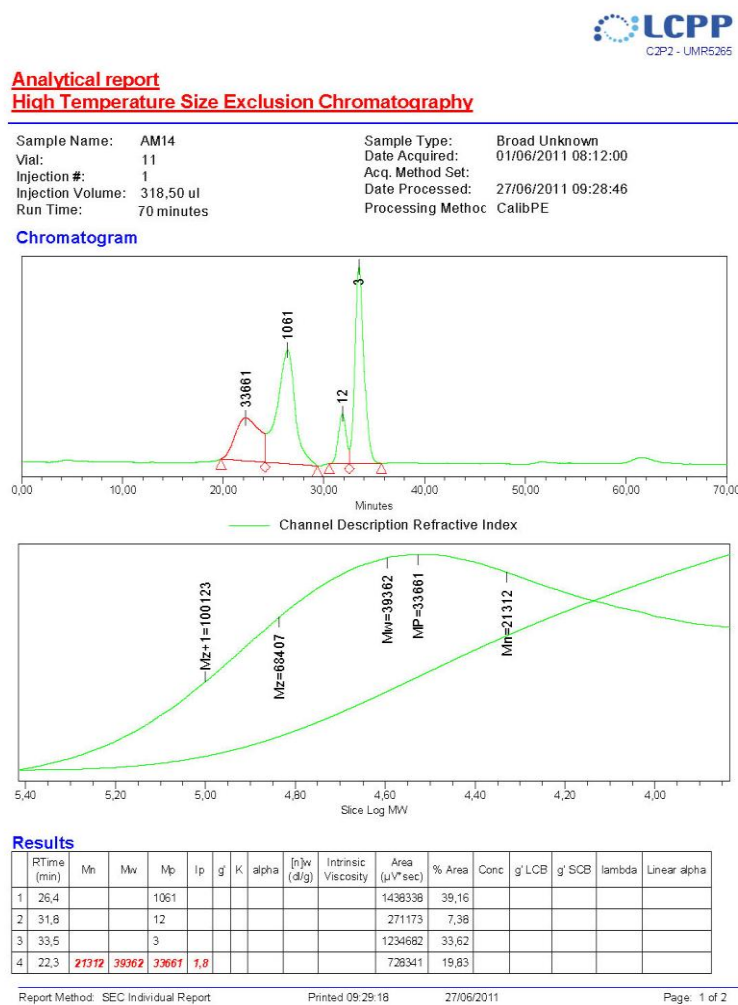


Figure 37: SEC data for run 12 (Table 3)

**Results**

Linear K (dl/g)
1
2
3
4

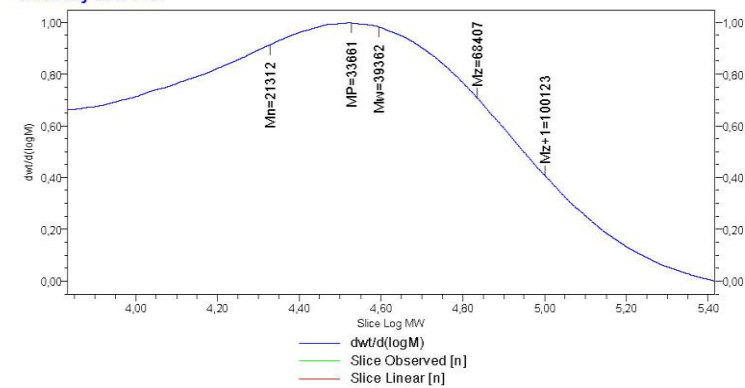
Viscosity Law Plot

Figure 38: SEC data for run 14 (Table 4)

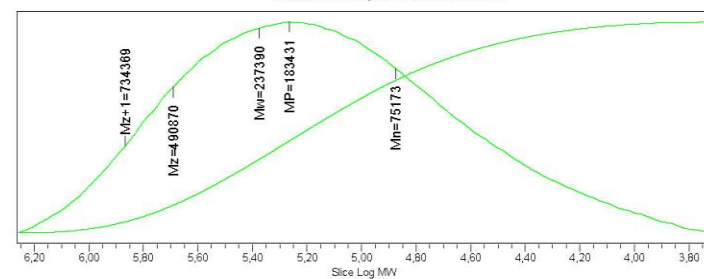
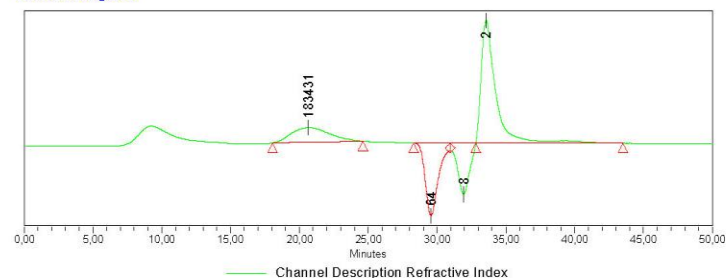


Analytical report High Temperature Size Exclusion Chromatography

Sample Name: AM26
Vial: 17
Injection #: 1
Injection Volume: 318,50 ul
Run Time: 70 minutes

Sample Type: Broad Unknown
Date Acquired: 25/08/2011 09:06:00
Acq. Method Set:
Date Processed: 31/08/2011 10:27:23
Processing Method: CalibPE

Chromatogram



Results

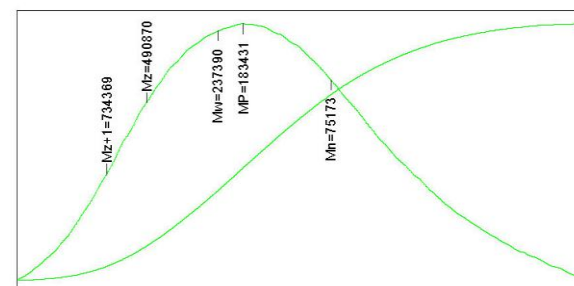
	RTTime (min)	Mn	Mw	Mp	Ip	g'	K	alpha	[η]v (dl/g)	Intrinsic Viscosity	Area (μV*sec)	Conc
1	20.6	75173	237390	183431	3.2						242953	
2	29.6			64							395235	
3	33.6			2							780106	
4	31.9			8							257686	

Report Method: SEC multi Report

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Report Method: SEC multi Report

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Figure 39: SEC data for run 15 (Table 4)

