Polymerization of methyl acrylate and as comonomer with ethylene using single-site catalysts

Sameer S. Vadhavkar
Polymerization of Methyl Acrylate and as Comonomer with Ethylene Using Single-Site Catalysts

By

Sameer S. Vadavkar

A Thesis Submitted

in Partial Fulfillment

of the Requirements for the Degree of

Master of Science

in

Materials Science and Engineering

Approved by:

Prof. ________________________________

Dr. Massoud Miri (Thesis Advisor)

Prof. ________________________________

Dr. KSV Santhanam (Head of Department)

CENTER FOR MATERIALS SCIENCE AND ENGINEERING

COLLEGE OF SCIENCE

ROCHESTER INSTITUTE OF TECHNOLOGY

ROCHESTER, NEW YORK

MARCH 2008
Polymerization of Methyl Acrylate and as Comonomer with Ethylene Using Single-Site Catalysts

By

Sameer S. Vadhavkar

I, Sameer S. Vadhavkar, hereby grant permission to the Wallace Memorial Library of the Rochester Institute of Technology to reproduce this document in whole or in part that any reproduction will not be for commercial use or profit.

__________________________________________   ____________________________________________
Sameer S. Vadhavkar                                    Month, Date, Year
This volume is the property of the Institute, but the literary rights of the author must be respected. Please refer to permission statement in this volume for denial or permission by author to reproduce. In addition, if the reader obtains assistance from this volume, he must give proper credit in his own work.

The following persons, whose signatures attest to their acceptance of the above restrictions, have used this thesis.

<table>
<thead>
<tr>
<th>Name</th>
<th>Address</th>
<th>Date</th>
</tr>
</thead>
</table>
DEDICATION

I would like to dedicate this work to my parents, Dr. Savita Vadhavkar and Sunil Vadhavkar, without whom I would not be where I am today.
ACKNOWLEDGEMENTS

I would like to thank my advisor, Prof. Massoud (Matt) J. Miri, for his valuable guidance and support. His passion for chemistry and commitment to excellence has made my time at the Rochester Institute of Technology a truly remarkable experience.

I would also like to thank the members of Dr. Miri’s group both past and present. In particular, the friendship and enthusiasm of Matt Fullana and James Soucy ensured that each day was not only productive, but also enjoyable. Also would like to thank one of my research group members, Nikhil Kolhatkar, who has helped me a lot with my experimental part.

I would also like to thank my committee members Dr. Gerald Takacs and Dr. Thomas Smith for their time and research suggestions.

This research work was supported by the University Affairs Committee foundation grant of Xerox Corporation. So I would like to thank Dr. G. Sacripante of the Xerox Research Centre of Canada for his support.

The GPC measurements were made by Dow Chemical Corporation, so I would like to thank Dr. Peter Nickias for providing the data.

Finally special thanks to my parents, Dr. Savita Vadavkar and Sunil Vadavkar and my brother, Swapnil Vadavkar. My accomplishments have only been possible with their support, and this thesis stands as a testament to their dedication.
Title of Document: POLYMERIZATION OF METHYL ACRYLATE AND AS COMONOMER WITH ETHYLENE USING SINGLE-SITE CATALYSTS
Sameer Sunil Vadhavkar, Master of Science, 2008

Advisory Committee: Dr. Massoud (Matt) Miri,
Dr. Thomas W. Smith
Dr. Gerald A. Takacs

Because of the excellent control over polymerizations provided by single-site catalysts (SSCs), numerous research groups are trying to find such catalysts, which would also be efficient for the polymerization of polar monomers. However, many SSCs are deactivated by undergoing reactions with the electronegative atoms in the polar groups. In the present work, we attempted to copolymerize ethylene with methyl acrylate using three SSCs: (1) a bis(imino)pyridyl iron(II) chloride / methylaluminoxane catalyst, (2) a chiral metallocene / tris(pentafluorophenyl) borane catalyst, and (3) an in situ trifluoromethyl substituted nickel (II) enolate catalyst. Only the first two catalysts led to polymer formation. The metallocene had relatively low activities and formed polymethyl acrylate. The most efficient catalyst for the synthesis of the copolymers was the iron-based catalyst 1. The ethylene consumption indicates that its activity reaches a maximum after which it steadily declines. By kinetic measurements, $^1$H and $^{13}$C NMR spectroscopy and the measurement of glass and melting temperatures, we could show that copolymers of ethylene and methyl acrylate were not formed. The products formed were blends, of high density polyethylene and methyl acrylate. Homopolymerizations of methyl acrylate using the three catalyst systems were also studied. Again it was found that the catalyst 1 had the highest activities. Atactic polymers were formed. There was a clear dependence of the activity and molecular weight on the Al/Fe-ratio, which indicates that the polymerization mechanism is coordinative and not initiated by radical species.
MAIN RESEARCH GOALS AND SUMMARY OF RESULTS

The main goal of this research is to find a single-site catalyst system, which can form copolymers of ethylene and methyl acrylate. Single-site catalysts represent the most recent generation of Ziegler/Natta catalysts, which in contrast to the latter only form one active catalytic species. Copolymers of ethylene with polar monomers are used as adhesives, paints and compatibilizers. Historically, these copolymers have only been prepared by free-radical copolymerization. Now there is potential for the use of coordination systems as well (i.e. single-site catalyst). Single-site catalysts not only provide an excellent control over tailoring properties of polyolefin but also provide better incorporation with higher yields. The single-site catalysts based on late transition metals appear to be more stable towards polar group monomers. For our experiment we are considering a modified metallocene catalyst, an iron based bis(imino)pyridine catalyst and a nickel(II)enolate. Our work also includes characterization of the copolymers by IR, $^1$H NMR, $^{13}$C NMR, TGA, DSC, and GPC, the latter provided by Dow Chemical.

In this work, the homopolymerization of methyl acrylate (MA) and its attempted copolymerization with ethylene using three single-site catalysts is described. The primary catalyst under investigation is formed from a bis(imino)pyridine iron(II) chloride with methylaluminoxane (1), which is compared to bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dimethyl / tris(pentafluorenyl)borane) (2), and a P,O-chelated nickel(II) enolate catalyst (3). Catalyst (1) leads to the highest activities exceeding those of catalyst (2) by a magnitude. Catalyst (3) results in formation of no polymer. The kinetics of the
polymerizations and the effect of the Al/Fe-ratio and temperature on the activity and molecular weight of the polymers have been determined. In the ethylene/methyl acrylate copolymerization trials, catalyst (1) produces a blend of the two homopolymers, polymethyl acrylate (PMA) and polyethylene, catalyst (2) forms PMA only, and catalyst (3) results again in no polymer formation. Remarkably, using catalyst (1) it is possible to produce polymer blends with up to 52 % PMA at high activities. The polymerization kinetics has been determined based on the directly measured uptake of ethylene during the runs. $^1$H NMR and DSC have been used as efficient methods to prove that polymer blends instead of true copolymers were formed. Finally, the polymerization mechanism will be discussed.
# TABLE OF CONTENTS

Dedication........................................................................................................................................ 4  
Acknowledgement.................................................................................................................................. 5  
Abstract................................................................................................................................................ 6  
Main Research Goals and Summary of Results ............................................................................. 7  
Table of Contents................................................................................................................................. 9  
List of Figures.......................................................................................................................................... 10  
List of Schemes.................................................................................................................................... 12  
List of Tables......................................................................................................................................... 13  

Chapter I – INTRODUCTION TO ZIEGLER-NATTA CATALYSTS................................................... 14-34

  History and Introduction.................................................................................................................. 15
  Evolution of Single-Site Catalysts.................................................................................................... 17

Chapter II – EXPERIMENTAL PROCEDURE............................................................................... 35-50

  Materials.............................................................................................................................................. 36
  Synthesis of Iron Based Catalyst....................................................................................................... 37
  Synthesis of Nickel Based Catalyst................................................................................................... 40
  Experiment Set Up............................................................................................................................ 42
  Distillation Set Up and Procedure.................................................................................................... 45
  Polymerization of Ethylene................................................................................................................ 47
  Polymerization of Methyl Acrylate.................................................................................................... 48
  Copolymerization of Ethylene / Methyl Acrylate........................................................................... 49
  Polymer Characterization................................................................................................................... 50

Chapter III – RESULTS.................................................................................................................. 51-77

  Part I: Attempt to Copolymerize Ethylene with Methyl Acrylate.............................................. 52
  Part II: Homopolymerization of Methyl Acrylate.......................................................................... 66

Chapter IV – DISCUSSION............................................................................................................. 78-81

Chapter V – CONCLUSIONS......................................................................................................... 82-83

Chapter VI - REFERENCES.................................................................................................................. 84-87
LIST OF FIGURES

1) Zirconocene dimethyl – one of the first metalloccenes applied as polymerization catalyst.................................................................21
2) Ethylene bis(indenyl) zirconium dichloride........................................22
3) Isotactic and Atactic Polypropylene.....................................................24
4) Three possible orientations of the chiral metallocene catalyst with the polymer chain and the incoming monomer..............................25
5) Fluorenyl Catalyst..............................................................................26
6) Synthesis of Ligand for the Iron Catalyst..............................................34
7) Synthesis of Complex for the Iron Catalyst..........................................35
8) In situ catalyst preparation with tetrachlorobenzoquinone..................35
9) Experimental manifold setup................................................................43
10) Polymerization apparatus..................................................................44
11) Distillation setup................................................................................46
12) Polymerization rate based on ethylene consumption versus polymerization time..................................................................54
13) Typical IR spectrum of a copolymer.....................................................57
14) Peak assignments in H NMR spectra....................................................58
15) H NMR spectra for the copolymer.......................................................59
16) Peak assignment for the C 13 NMR spectra........................................60
17) C 13 NMR for the copolymer..............................................................61
18) Typical TGA spectrum for the copolymer..........................................62
19) Typical DSC spectrum for a copolymer.................................................................63

20) Kinetic plot for polymerization of methyl acrylate with catalysts 1 and
    2........................................................................................................................................67

21) Dependence of Polymerization activity on Al/Fe-ratio........................................68

22) Influence of the number average molecular weight on Al/Fe-ratio.....................69

23) Influence of the polydispersity index on Al/Fe-ratio...........................................70

24) H NMR of a polymethyl acrylate measured in CDCl3.......................................71

25) H NMR spectra’s for Poly Methyl Acrylate made with catalyst 1 and 2.........72

26) Influence of the Al/Fe-ratio on tacticity of polymethyl acrylate with catalyst
    1...........................................................................................................................................72

27) Influence of the degree of tacticity of polymethyl acrylate on temperature.......74

28) Influence of the Al/Fe ratio on tacticity of polymethyl acrylate with catalyst
    1...........................................................................................................................................76

29) Influence of the degree of tacticity of polymethyl acrylate on temperature.......76
LIST OF SCHEMES

1) The Arlman - Cossee mechanism for a heterogeneous Ziegler/Natta catalyst… .19
2) Mechanism of Ziegler-Natta Polymerizations………………………………………20
3) Activation of CP₂TiCl₂ by………………………………………………………………………………23
4) Mechanism of MAO activation……………………………………………………………..27
5) Cossee-Arlman mechanism for metallocene polymerization…………………………….28
6) Syndiotactic polymethylmethacrylate…………………………………………………………31
7) Isotactic polymethylmethacrylate……………………………………………………………31
8) E/MMA Copolymer made with a α-Diimine Palladium Catalyst……………………….32
9) Proposed formation of the catalyst precursor Tetrachlorobenzoquinone………………36
10) Proposed pathways for the simultaneous polymerization of methyl acrylate and ethylene by the iron based catalyst (1)……………………………………………………………81
LIST OF TABLES

1) Worldwide production of polyethylene.................................................................15

2) Leading companies in metallocene technology and their processes..................16

3) Conditions and activities for the copolymerization of Ethylene/Methyl Acrylate..................................................................................................................53

4) Selected glass transition temperatures of homopolymers, “copolymer”-blends produced with (I), and a true copolymer made with AIBN from DSC measurements.......................................................................................................64

5) Conditions and activities for the polymerization of methyl acrylate with three single-site catalysts.................................................................................................66

6) Percentages of racemo and meso diads in dependence of main polymerization parameters.......................................................................................................................75
CHAPTER I

INTRODUCTION TO ZIEGLER-NATTA CATALYSTS
HISTORY AND INTRODUCTION

Ziegler-Natta type catalysts are widely used to produce high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polypropylene (PP), and ethylene-propylene-diene monomer (EPDM) and many more types of Ziegler-Natta catalysts have been developed and used for the mass production of polymers. The table below shows the worldwide production of HDPE, LLDPE and low density polyethylene (LDPE), in the past years.²

Table 1: **Worldwide Production of Polyethylene**²

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>7,643</td>
<td>7,784</td>
<td>7,691</td>
<td>7,578</td>
<td>8,023</td>
<td>7,987</td>
</tr>
<tr>
<td>LDPE</td>
<td>5,243</td>
<td>6,361</td>
<td>6,888</td>
<td>7,227</td>
<td>9,508</td>
<td>9,907</td>
</tr>
<tr>
<td>LLDPE</td>
<td>11,211</td>
<td>12,373</td>
<td>12,557</td>
<td>12,924</td>
<td>15,182</td>
<td>15,423</td>
</tr>
</tbody>
</table>

Table 2 shows the leading manufacturers of polyethylene and polypropylene and the proprietary processes used in their production.
Table 2: Leading Companies in Metallocene Technology and Their Processes

<table>
<thead>
<tr>
<th>Company</th>
<th>Process/Technology</th>
<th>Typical Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>ExxonMobil</td>
<td>Exact</td>
<td>it-PP</td>
</tr>
<tr>
<td>Dow</td>
<td>Insite</td>
<td>m-LDPE</td>
</tr>
<tr>
<td>Basell</td>
<td>Avant</td>
<td>it-PP</td>
</tr>
<tr>
<td>Hoechst/Mitsui</td>
<td>Topas</td>
<td>Topas</td>
</tr>
<tr>
<td>Atofina</td>
<td>Finacene</td>
<td>st-PP</td>
</tr>
</tbody>
</table>

Single-site catalysts represent the state-of-the-art Ziegler-Natta catalysts. At the end of seventies, the discovery of homogeneous single-site metallocene catalysts was one of the major breakthroughs in the polymer producing industries. This led to the production of new modified and superior polymers. In the late eighties, another group of single-sites catalysts based on diimine complexes of late transition metals, such as nickel and cobalt, were discovered, which also produced polyolefins at very high activities.¹
EVOLUTION OF SINGLE SITE CATALYSTS

During the period of 1900-1953, a number of research groups were actively involved in organometallic chemistry. In 1930 Marvel and Friedrich found that ethylene was polymerized to low molecular weights in presence of lithium alkyls. Using this as a basis, Ziegler and co-workers investigated the mechanism by which alkali metal alkyls initiated the polymerizations. They speculated that the ether-soluble LiAlH$_4$ could also serve as a source of lithium alkyl. They demonstrated that LiAlH$_4$ reacted with ethylene to form LiAlEt$_4$. Initially they thought that ethylene would polymerize only on the LiEt portion and not on AlEt$_3$, but later found out that AlEt$_3$ polymerized ethylene even more efficiently.

After this discovery, Ziegler and Gellert switched to AlEt$_3$. The equilibrium between metal alkyl and metal alkyl hydride plus olefin components could now be established since all of the metal alkyl and metal alkyl hydride components remain soluble. This feature made it possible for Ziegler and Gellert to study the organometallic synthesis of olefins. Ziegler and Breil next examined a series of transition metal salts in combination with AlEt$_3$ in an effort to find other displacement catalysts. Transition metal salts (groups IV to VI) were also active, but the most active catalyst was made from TiCl$_4$ and AlEt$_3$, and this was developed for large-scale production of high-density polyethylene plastics. Later, Ziegler informed his discovery of the catalyst to Montecatini Company (Italy) and Goodrich Gulf Chemical Company (USA).
In early 1954, the Natta group carried out their first successful experiment with the Mulheim catalyst and found that with crystalline modifications of beta- and gamma-titanium trichloride in combination with diethyl aluminum chloride, a mixture of amorphous and crystalline fraction polypropylenes was produced. The overt experiment was made at the end of 1953 by Ziegler and his co-workers in which ethylene reacted with AlEt₃ and zirconium acetylacetonate. The white powder, which filled the autoclave, was a high molecular weight, linear polyethylene.

In 1955 Vanderberg at Hercules (32) and Ettore and Luciano at Montecatini discovered that the molecular hydrogen acted as a true transfer agent for the Ziegler-Natta catalyst. This was a very important discovery because many of the Ziegler-Natta catalysts produce polymers whose molecular weights are too high. Ziegler-Natta catalysts typically contain a salt or metal-organic compound of titanium, zirconium, vanadium, chromium, nickel, cobalt, as catalyst, and an aluminum alkyl as a cocatalyst.

The following scheme shows the coordination of the catalyst with the cocatalyst. An alkyl exchange between the cocatalyst and the transition metal salt occurs in order to form the active catalyst.
For e.g.

\[
\begin{align*}
\{ & \text{TiCl}_4 \quad + \quad \text{AlEt}_3 \quad \Rightarrow \quad \text{TiCl}_3\text{Et} \quad + \quad \text{AlEt}_2\text{Cl} \} \\
\end{align*}
\]

(Et: ethyl = C\(_2\)H\(_5\))

**Scheme 1:** The Arlman - Cossee mechanism for a heterogeneous Ziegler/Natta catalyst\(^3\)

The first step shown in scheme 1 is the complexation step of the monomer to the transition metal complex where the d-orbitals of the transition metal overlap with the pi-bonds of the olefins. The second step shows the formation an electron deficient four-membered ring. Third step is the insertion step where the monomer is inserted between the transition metal atom and the carbon atom of the alkyl group occurring as a syn-addition. Finally, a “migration” step takes place, in which the alkyl group and the vacant site go back to their original position. For obtaining an isotactic polymer, the next monomer must undergo complexation and insertion after the migration occurs.
In 1965, H. Sinn at the University of Hamburg conducted research on homogeneous Ziegler-Natta catalysis with simple metallocenes as catalysts such as biscyclopentadienyl zirconium dichloride. These first generation metallocene catalysts have the tendency to produce ethylene copolymers of lower molecular weights.\textsuperscript{4} Homogeneous Ziegler/Natta catalysts appeared more feasible for kinetic studies. Sinn and Kaminsky studied the structures of these catalyst compounds and their reactions with ethylene. It took 15 years for them to study their detailed kinetics, which is demonstrated in the following scheme.

\textbf{Scheme 2: Mechanism for Homogeneous Ziegler-Natta Catalysts}\textsuperscript{4}
Initially a complexation of the monomer and the metal complex takes place followed by insertion of the monomer (first step shown). A β-hydrogen atom is transferred from the alkyl group of the other transition metal resulting in the evolution of ethane, proceeding to the ultimate reduction and deactivation step. Zirconium is preferred over titanium as metal center because of its lower tendency to reduction. Therefore the perfect combination for a Ziegler-Natta system should be Cp₂Zr(CH₃)₂ with Al(CH₃)₃, because the side reactions leading to catalyst deactivation would be minimal.

An example of the structure of metallocene compound is shown below in Figure 1.

![Zirconocene dimethyl](image)

**Figure 1:** Zirconocene dimethyl – one of the first metallocenes applied as polymerization catalyst
However, later it was found out that this combination was not suitable for polymerization of ethylene, as it did not remain active. But students who were less experienced with Schlenk systems in protecting the catalyst compounds from poisons such as water and oxygen, accidentally obtained higher polymerization activities.

Sinn and Kaminsky found that a more active catalyst system was formed as relatively small amounts of water, which were present in the moisture in the air, reacted with trimethylaluminum. For subsequent polymerizations they produced the reaction product of the aluminum alkyl and water, called methylaluminoxane (MAO). The reaction was as follows:

\[
\text{n} + 1 \quad \text{Al} (\text{CH}_3)_3 + \text{n} \, \text{H}_2\text{O} \rightarrow \text{CH}_3\left[\begin{array}{c}
\text{CH}_3 \\
\text{Al} - \text{O}
\end{array}\right]_{\text{n}} \text{Al}_\text{K} \text{CH}_3 + 2\text{n} \, \text{CH}_4
\]

This new MAO cocatalyst boosted the activities to very high levels and later was termed as first superactive metalloocene catalyst, which was a combination of \( \text{Cp}_2\text{ZrMe}_2 \) with MAO.\(^4\)

This appeared to be the first Ziegler-Natta type catalyst which had no halogen atom in it. This was considered as a prerequisite for catalyst activity. The activities of the first metalloocene generation catalysts were very high as compared to those of the best industrial Ziegler-Natta catalysts, e.g. 30,000 kg PE/gZr. It could also be shown that the other monomers could be copolymerized with ethylene such as 1-hexene, forming LLDPE, and with propylene leading to EPDM elastomers.\(^5\) However, these early metalloocene catalysts only led to the formation of atactic polypropylene (at-PP).
The activation of the metallocene by a cocatalyst is shown in the following scheme.

**Scheme 3:** Activation of $\text{CP}_2\text{TiCl}_2$ by $\text{AlEt}_3$

In 1985, discovery of the chiral and rigid metallocenes was made by Ewen at Exxon and Kaminsky. These metallocenes led to the formation of isotactic polypropylene. Brinzinger at the University of Konstanz had already synthesized using these catalyst systems. For example ethylene bis(indenyl) zirconium dichloride, which is shown below. These bridged metallocene catalysts typically result in polymers with higher molecular weights.\(^6\)

**Figure 2:** *Ethylene bis(indenyl) zirconium dichloride*
The catalyst consisted of a two-ring system made of a cyclopentadienyl ring that is fused to an indenyl ring and an ethylene bridge connected to the aromatic ring ligands. If the ethylene bridge were not there then the ligands would swivel around and might not stay pointed in the right direction to lead to isotactic polymerization. The big bulky indenyl ligands guide the incoming monomer for the insertion and point in opposite directions as shown in the figure above.

![Isotactic and Atactic Polypropylene](image)

**FIGURE 3: Isotactic and Atactic Polypropylene**

The racemic mixture result in high degrees of isotactic polypropylene and the meso-form leads to atactic polypropylene as shown in the above figures. The racemic form of the catalyst has a C2 –symmetry. As shown in fig 4, the monomer can approach the specific enantiomer from any side (because of its symmetry it does not matter). It could either be the R or the S form. The propylene always approaches the specific catalyst site with the same enantiotropic face, i.e. Re-face or Si-face.
Figure 4: Three possible orientations of the chiral metallocene catalyst with the polymer chain and the incoming monomer. Among these A is the most preferred, most importantly because the polymer chain is the furthest away from the methyl group of the incoming propylene.⁶

One major breakthrough for the commercialization of metallocenes as a catalyst was the production of highly crystalline form of polypropylene with a soluble Ziegler-Natta catalyst.

Later, a rigid fluorenyl cyclopentadienyl zirconium catalyst was designed by Ewen at Exxon and Razavi to produce highly syndiotactic polypropylene. The fluorenyl catalyst has a Cs-symmetry with a mirror plane going horizontally through the molecule as shown in fig 4. The methyl group of the incoming propylene is forced to come in
between the two six rings of the fluorenyl group due to the bulky wings present in the fluorenyl ring structure. On one side of this catalyst the Re-enantiotropic face will be added, and the on the opposite side Si-face is added. Since with every insertion the polymer chain changes its position syndiotactic polypropylene will be formed. When a bulky group is present at the β-position (group such as a tertiary butyl), the propylene is forced to add only from one side. In this case a racemic isotactic polypropylene is formed.⁷

Figure 5: Fluorenyl catalyst

One of the important parts of the metallocene catalysts is the co-catalyst methyl aluminoxane (MAO). The methyl group from MAO plays an important role in the alkylation process of the catalyst as it removes chlorine giving the zirconium a positive charge. This charged complex is stable as the electron from the carbon-hydrogen bond is shared with the zirconium. The following reaction shows how the catalyst works with co-catalyst to yield the cation complex.
\[
\left\{ \begin{array}{c}
\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl} + [\text{Al}(\text{CH}_3)\text{O}]_n \\
\to \text{Cp}_2\text{Zr'}\text{CH}_3 + [\text{Al}(\text{CH}_3)\text{ClO}]^- + [\text{Al}(\text{CH}_3)\text{O}]_{n-1}
\end{array} \right\}
\]

**SCHEME 4: Mechanism of MAO activation**

The complete Cossee-Arlman based mechanism for a metallocene is explained in the scheme below.
Scheme 5: Cossee-Arlman mechanism for metallocene polymerization.\textsuperscript{8}

The cocatalyst (MAO) is shown on the left side of the scheme. Alkylaion stage takes place prior to complexation step. In the first stage, an α-agostic hydrogen and Π-complex is formed and this makes the complex stable. Then a four-membered ring is formed, and the complex becomes electron deficient. The bond is rearranged to form a gamma-agostic product. The complex flips back with a vacant site and in the opposite position to the reagent in the first reaction step. With every insertion the polymer chain flips back to the other side. Also the vacant site changes sides compared to the active catalyst of the previous insertion step.
The polymerization of polar monomers with metallocene catalysts does typically not result in high polymer yield. These polar compounds lead to a deactivation of the catalyst system, because of the reaction of the transition metal with electronegative atoms in the polar monomer. Most Ziegler Natta catalysts including the metallocenes are highly oxophilic that is they react with oxygen, in free form or bonded in polar compounds, to produce polymerization inactive species. Alcohol is typically used to terminate a polymerization. In particular, the presence of strong acids result in the formation of aluminum compounds, which are ineffective for the polymerizations. Also high amounts of water can hydrolyze the metallocenes.

Yasuda found that the metal-organic compounds of rare earth metals, such as yttrium, can be as promising catalysts for polymerization of polar monomers, such as methyl methacrylate. High molecular weight PMMA with narrow polydispersity was also obtained by using [SmH(C₅Me₅)₂]₂ and LuMe(C₅Me₅)₂(THF) catalysts.⁸,⁹ The syndiotacticity of the methacrylate group decreased as the bulkiness of the alkyl group increased. At lower temperatures, 95% of syndiotactic polymer was obtained. The organo-lanthanide complexes caused the formation of polymers at high conversions within a short time period.

The rare transition metal compound Me₂Si(C₅Me₅) (C₅H₄-1S, 2S, 5R-neomenthyl)Lar (R = CH(Me₃Si)₂ produced isotactic poly(methyl methacrylate).⁹ However, these catalysts are also more sensitive to moisture and generally not as stable as most metallocenes. This is one of the main reasons for their lower polymerization activities.
Late transition metal such as Pd(II) and Ni(II) with α-diiimine ligands have enabled the production of high molar mass polymers with both ethylene and 1-olefins. The ability to produce highly branched ethylene polymers and potentially copolymerize ethylene with other polar monomers is one of the most unique features of these late metals.

In 1992, Collins and Ward produced syndiotactic poly(methyl methacrylate) with a narrow molecular weight distribution by using Cp₂ZrMe₂ and [Cp₂ZrMe(THF)][BPh₄] at room temperature.¹⁰ The polymerization had moderate activity. Also they found that the effective initiators for living polymerization of methyl methacrylate initiated the polymerization.¹⁰

Collins and Ward also showed by using Cp₂ZrMe₂ at room temperature that metallocenes catalysts could polymerize methyl methacrylate. A highly syndiotactic polymethylmethacrylate was produced with a molecular weight of (Mw = 50 – 200,000 g/mole), and molecular distribution (MWD = 1.2 – 1.4).¹¹

In 1992, Yasuda and Yamaoto used group 3B lanthanides complexes [Cp*₂SmH]₂ and [YMe(C₂H₅)₂]₂, to obtain syndiotactic polymers with an extremely narrow molecular weight distribution (MWD = 1.05 – 1.02).
In 1994, Soga and his coworkers employed a complex of a Lewis acids such as diethyl zinc $[\text{Zn(C}_2\text{H}_5)_2]$ with the methyl methacrylate in combination with a metallocene catalyst to form the isotactic-PMMA. $^9$

The deactivation of the metallocene metal center through the strong interaction of the additives with the functional ester group of monomer in the reaction is prevented by diethyl zinc. This combination allowed for the usage of a lower amount of MAO.
Brookhart discovered that the palladium (II) and Nickel (II) based catalysts could be used to polymerize ethylene and propylene with high activity.\textsuperscript{12} The α-diimine catalysts shown in Scheme 8 also produced poly-α-olefins of high molecular weights. Due to the nature of late transition metal catalysts, they are expected to be more tolerant towards functionalized vinyl monomers. According to Correia only Pd (II) with α-diimine ligands could catalyze copolymerization of ethylene with functional monomer and with monomer that do not have acidic hydrogen.\textsuperscript{13}

**SCHEME 8**: E/MMA Copolymer made with α-Diimine Palladium Catalyst

OPTEMA\textsuperscript{10} is a series of co-polymers of ethylene / methylacrylate produced by the Exxon Mobil Chemical Company. The OPTEMA TC020 and TC120 contain up to 21 wt % methyl acrylate and are used for seaming, heavy-duty shipping sacks, pond liners, medical packages, agricultural, and construction films.\textsuperscript{9}
Recently, Gibson and Brookhart discovered new catalysts based on pyridine-diimine complexed of Fe(II) and Co(II).\textsuperscript{13} These catalysts could be even less electrophilic and oxophilic than the α-diimine complexes of Ni(II). At the end of the nineties, Brookhart and Gibson reported that iron(II) & (III) and cobalt(II) complexes with 2,6-bis imino pyridyl ligands were highly active. These later catalysts have a good potential to be active for our target polymers. The iron complexes represent a new class of isospecific propylene polymerization catalysts.\textsuperscript{15}

These catalysts are unique in several ways. They are the first late-metal systems known to polymerize propylene in an isotactic fashion. Regardless of catalyst structure, the isotacticity is governed by a chain-end control mechanism. Second, chain propagation proceeds through 2,1 insertion of monomer, making these the first isospecific propylene polymerization catalysts that operate via a secondary enchainment mechanism. Third, the polymer end groups resulting from termination consist solely of 1-propenyl groups, making these the first systems to produce only α-olefins end groups by β-H elimination from the growing polypropylene chains. Finally, these polymers are highly regioregular, with regioerrors occurring only in the lower molecular weight polymers made by the complexes with reduced steric bulk.

Xuan Mai, a former graduate student in Dr. Miri’s group, wrote his thesis on initial work on copolymerizations of ethylene with methyl acrylate. However, he used only relatively low concentrations of methyl acrylate, not exceeding 1 mol % in the polymer. The polymer products appeared very similar to copolymers. Our primary goal in this work is to investigate the polymerizations at high ratios of acrylate to ethylene.\textsuperscript{42}
In the following I am describing the syntheses of two of the catalyst compounds, which are commercially not available and we produced by using literature procedure as indicated.

**Synthesis of Iron Catalyst**

2,6-diacetylpyridine(2,4,6-trimethylanil) Iron(II)chloride / methylaluminoxane;

\{2, 6 Diacetylpyridine (2, 4, 6 – trimethylanil) Iron(II)chloride\}

1. Synthesis of Ligand

![Figure 6: Synthesis of Ligand](image-url)
2. Synthesis of Complex

**Figure 7: Synthesis of Complex**

**Synthesis of Nickel Catalyst**\(^4^3\)

trifluoromethyl substituted P\(^\alpha\)O chelated nickel enolate / none

Synthesis of In-situ Phosphine Enolate Ni Complex.

**Figure 8: In situ catalyst preparation with tetrachlorobenzoquinone**\(^4^3\)
Scheme 9: Proposed formation of the catalyst precursor Tetrachlorobenzoquinone$^{43}$
CHAPTER II

EXPERIMENTAL PART
MATERIALS

Argon (99.995% pure) was obtained from Airgas and was used without further treatment. Most materials were obtained from Sigma-Aldrich. A 10% toluenic solution of methyl aluminoxane (MAO) was obtained from Chemtura. The dimethylsilyl bis(tetrahydro-1-indenyl) zirconium(IV) was purchased from MCAT, Germany. The polymerization solvent toluene was distilled by refluxing over sodium with benzophenone. Methyl acrylate was degassed and dried over molecular sieve. Usually the distilled methyl acrylate led to its self-initiated polymerization. We avoided distilling methyl acrylate for our polymerizations. The bis(imino(pyridyl iron(II) chloride catalyst and the trifluoromethane bearing nickel enolate catalyst were synthesized according to a literature procedure. 19,20

Catalyst / Co-catalyst I:

2,6-diacetylpyridine(2,4, 6 – trimethylanil) Iron(II)chloride / methylaluminoxane

Catalyst / Co-catalyst II:

rac-dimethylsilylbis(4,5,6,7–tetrahydro–1–indenyl) zirconium
dimethyl/tris(pentafluorophenyl) borane

Catalyst / Co-catalyst III:

trifluoromethyl substituted P^O chelated nickel enolate / none
SYNTHESIS OF IRON BASED CATALYST (1)

Chemicals used for the synthesis of ligands

2, 6 – Diacetylpyridine - 3.0259 g
Ethanol (absolute) - 50.0 ml
Trimethylaniline - 5.2 ml
Glacial acetic acid - 10 drops

All operations are performed under argon

Procedure:

- 3 neck flask is prepared with 3 Vac/Ar cycles and equipped with magnetic stirrer and thermometer (up to 100C)
- All these chemicals above are mixed and then allowed to reflux overnight at 78 C
- Next day the solution was collected and cooled
- The solution upon cooling formed yellow crystals on bottom of flask
- These crystals were extracted and washed using cold ethanol

Synthesis of Complex

Chemicals used for synthesis of complex

1-butanol - 50.0 ml
Iron(II) chloride pellets (anhydrous) - 0.986 g
All operations are performed under argon

Procedure:

- The above 2 compounds were mixed in a 3 neck flask and stirred until the pellets dissolve at 85 C for about an hour
- The ligand was then added to the solution in small amounts while stirring this solution turned dark blue
- After stirring the solution was cooled and then concentrated to a volume of about 75 ml using a modified cold trap
- Diethylether was added to precipitate to a blue solid which was later washed and filtered using diethylether and a medium filler. The catalyst was dried and massed. (Total catalyst made = 2.2547 g)

The procedure for the metallocene catalyst is not given here because it was available commercially.
Synthesis of In-situ Phosphine Enolate Ni Complex.

The toluene was dried over sodium and the methanol over magnesium.

*All operations are performed under argon*

Procedure:

- The TCBQ was dissolved with the triphenylphosphine in 5 ml toluene (at high concentrations – with recipes with quantities of each 8.0 mmol or above ca. 300 μmol/ml of the phosphine and the quinone in 30 ml toluene – rust like red precipitate formed. Otherwise an orange solution formed.)

- After adding 1 ml of methanol, a dark red solution was obtained, which after stirring for about 20 min lightened up to yellow-orange.

- This solution was transferred to the solid Ni(COD)$_2$. This lead to a color change to lemon like yellow.

- This solution of the in-situ catalyst was directly used in the polymerizations.
EXPERIMENT SET UP

All the polymerizations were carried out in a Buchi autoclave as it had several advantages over other reactors. As shown in the figure 10, the Buchi autoclave has 2 jackets, the inner jacket, inside of which all the reactions take place, and an outer jacket, which is used for cooling purpose. Using an external water bath which pumps water between the outer and inner jackets controls the temperature of the reactor. An external engine drives an internal magnetic stirrer. The main purpose of using a magnetic stirrer is to eliminate the need for gaskets and specialized bearings to keep the pressure constant inside the reactor. It also keeps the internal atmosphere free from environmental contamination.

A glass manifold is used for the vacuum and argon connections. A vacuum pump is connected to the manifold for generating vacuum in the system through a vacuum trap. This trap is immersed in liquid nitrogen to prevent solvent fumes from being pulled in to the pump and possibly destroying the gaskets and internal workings of the pump. In order to protect the glassware from blowing, a mercury pressure bubbler is connected to keep the argon gas pressure around atmospheric pressures.
Figure 9: Experimental manifold setup\textsuperscript{42}
Figure 10: Polymerization apparatus
DISTILLATION SETUP AND PROCEDURE

All polymerization runs were carried out with distilled solvent (toluene). Also for the synthesis of Zirconium catalyst, we had to distill diethyl ether. In the distillation setup, the main reservoir is the three-neck flask, on top of which a distillation head is mounted. As shown in figure, the distillation column has two Teflon sleeves or valves. When the exit port valve is closed and the reflux valve was open, the system acted as a reflux apparatus. The toluene was refluxed overnight with sodium and benzophenone (ratio of sodium : benzophenone = 1 : 1.5). The boiling point of Toluene is around 130 °C (at 150 °C Toluene vaporizes and distillation starts). Diethyl ether is also distilled according to the same procedure. The boiling point of diethyl ether is 34.6 °C.

Most of the polymerization runs were carried out for 10-60 minutes to achieve low conversions, so that the monomer concentrations do not change significantly. As these polymerizations are exothermic in nature, the temperature changes rapidly, so we monitored these temperature changes. Even a 3-degree temperature change was considered to be a rapid change, which lead to a loss of control of the polymerization. This temperature change was controlled by an external cooling water bath. Most of the ethylene homopolymerizations were very rapid and highly exothermic, so the reaction time was reduced to almost around 5 minutes.

To complete the polymerizations the ethylene gas was turned off and ethanol was added to deactivate the catalyst and terminate the polymerization. Further methanol was added to the slurry to precipitate the polymer from the solution.
Figure 11: Distillation setup
POLYMERIZATION OF ETHYLENE

In case of iron catalyst, 250 ml of toluene and 2.3 ml of MAO were added to the reactor. The iron catalyst was premixed for 15 min. After 15 min of premixing the iron catalyst solution was added to the reactor and the temperature of the reactor was maintained around 20 °C. Ethylene flow was maintained at a pressure of 2 bars.

For ethylene polymerization with the nickel enolate catalyst, 180 ml of toluene was added to the reactor. 31.7 mg of Ni(COD)$_2$, along with CF$_3$ ligand to make the catalyst active, were transferred in to a 100 ml flask in the glove bag under argon. This flask had initially 10 ml of toluene in it. The catalyst solution was stirred for 15 min and was transferred to the reactor. Ethylene flow was started immediately at 4 bars pressure. Initially the solution in the reactor was yellow in color and hazy, later turning to a clear solution. Ethylene polymer was formed so quickly that the run had to be terminated after 2 min. Methanol was added to quench the polymerization. The ethylene polymerization was carried out at 55 °C but at the end of two min run the temperature went to 70 °C.
POLYMERIZATION OF METHYL ACRYLATE

The polymerization of poly methyl acrylate was carried out in a 100ml jacketed glass reactor, which was connected to an argon/vacuum inlet, a thermometer and a bubbler outlet. To start with, the reactor was heated to 70 °C and was evacuated three times using argon and vacuum. Initially, 17 ml of toluene is placed in to the reactor. The catalyst is premixed for 15 min., where 4 ml of toluenic solution of MAO and 4 mg of Fe-based catalyst were added. Just before starting the polymerization, 25 ml methyl acrylate was added in to the reactor. The polymerization temperature was maintained at around 60 °C and the run was carried out for 1 hour. 5ml methanol was added for the terminating the run. The slurry from the reactor was transferred to a beaker and ca 150 ml of methanol and hydrochloric acid were added and then stirred overnight. An amorphous and transparent solid product was obtained as it was dried overnight at 60 °C in the oven.

For the nickel based enolate catalyst system, the set up was the same. 23 ml of toluene was placed in to the 100 ml reactor. Later a 2 ml toluenic solution was added, in which 6.3 mg trifluromethane ligand precursor and 7.8 mg Ni(COD)$_2$ had been premixed for 15 min. 25 ml methyl acrylate was added in to the reactor and the polymerization was started.
COPOLYMERIZATION OF METHYL ACRYLATE AND ETHYLENE

For the copolymerization, the set up was the same as for the polyethylene synthesis. The polymerization run was carried out by two different methods of catalyst addition. In method I, most of the runs were carried out at 20 °C. Only in the case of nickel based enolate catalyst, in order to compare the activities, the runs were carried out at 60 °C. Initially toluene is added as a solvent at 20 °C in to the reactor. Then to the reactor, 20 ml of MAO and 10 mg of Fe based catalyst were added. The catalyst precursors were premixed for 15 minutes. Immediately to this, for example, 6.4 ml of methyl acrylate and ethylene was added. The reactor pressure was kept at 2 bars.

In the method II, the methyl acrylate was added after the toluene and before the MAO and Fe catalyst. The temperature and ethylene flow rate was monitored using Labview software from National Instruments. The ethylene flow was measured with a mass flow meter from Matheson based on thermal conductivity. At the end of the runs, methanol was added to quench the polymerizations. The polymer was filtered and washed with solution of dilute hydrochloric acid and methanol, and was stirred overnight.
POLYMER CHARACTERIZATION

A Differential Scanning Calorimetry (DSC) by TA instrument DSC 2010 was used to determine the thermodynamic properties such as the melting temperature of our polymers. The first heating cycle was kept at 20 K/min and second cycle was at 10 K/min.

Fourier Transform Infrared Spectroscopy was used to confirm the polymer composition. The spectra’s were recorded on a Biorad Excalibur FTIR FTS3000.

H NMR spectra were recorded on a Bruker DRX-300. For the H NMR spectra of polymethyl acrylate, CDCl$_3$ was used as a solvent, serving also as the reference. Probe concentrations were about 20 mg/ml. For the ethylene methyl acrylate copolymers the polymer were heated to 120 C in a 40/60 v/v-mixture of 1,2,4 trichlorobenzene (TCB) and d2-1,1,2,2-tetrachloroethane (C$_2$D$_2$Cl$_4$). NMR spectra were processed and graphed using a software program by Mestrec. C 13 NMR spectra were run on the same instrument at 75MHz and 120 °C for qualitative determinations.

DOW Chemicals provided the molecular weight properties. Polymethyl acrylate samples were based on calibration with poly methyl methacrylate standards, while the ethylene polymers were calibrated using polystyrene standards.
CHAPTER III

RESULTS
RESULTS

Part I: ATTEMPTS OF THE COPOLYMERIZATION OF ETHYLENE WITH METHYL ACRYLATE

During the copolymerizations of ethylene and methyl acrylate, we observed that the obtained polymer had properties and characteristics of a typical copolymer. This usually occurred at low concentrations of methyl acrylate. The spectroscopy showed us the presence of polymerized methyl acrylate next to polymerized ethylene. There was a decrease in the activity as the methyl acrylate concentration increased. Also the melting temperature of our polymer did not decrease as sharply as is expected temperature of copolymers. Gibson and co-workers had published earlier the formed polymers are not true copolymers, but rather are a blend of two homopolymers, HDPE and PMA\textsuperscript{33}. It was difficult for them to determine the formation of copolymer based in spectroscopy at low concentrations of acrylates. They separated the two homopolymers by applying solvent fractionation method.

We therefore wanted to investigate if there was any possibility to form copolymer also in the presence of high concentrations of methyl acrylate. We also were interested in finding a way to use NMR spectroscopy and the thermal properties of the polymer to determine what kind of polymer was formed. As shown in Table 3, we were able to actually get sufficiently high polymer yields even at very high ratios of the acrylates to ethylene.
Table 3 – Ethylene/Methyl Acrylate “Copolymerizations

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Cat.</th>
<th>Meth. of Addition for (I)</th>
<th>MA M</th>
<th>Cat. µmol</th>
<th>Cocat./Cat.-Ratio</th>
<th>t min</th>
<th>Yield g</th>
<th>Activit y a</th>
<th>MA in cop. mol-%</th>
<th>Mₘ b</th>
<th>PDI</th>
<th>Tm °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 c</td>
<td>(1)</td>
<td>A</td>
<td>0</td>
<td>1.2</td>
<td>2100</td>
<td>8</td>
<td>1.9</td>
<td>11875</td>
<td>0</td>
<td>83,245</td>
<td>21.7</td>
<td>134.7</td>
</tr>
<tr>
<td>2</td>
<td>(1)</td>
<td>A</td>
<td>0.1</td>
<td>21</td>
<td>1600</td>
<td>25</td>
<td>0.8</td>
<td>380</td>
<td>0.9</td>
<td>52,459</td>
<td>n.d.</td>
<td>128.0</td>
</tr>
<tr>
<td>3 d</td>
<td>(1)</td>
<td>A</td>
<td>0.3</td>
<td>17</td>
<td>1900</td>
<td>15</td>
<td>3.3</td>
<td>350</td>
<td>2.5</td>
<td>29,115</td>
<td>2.4</td>
<td>130.3</td>
</tr>
<tr>
<td>4</td>
<td>(1)</td>
<td>A</td>
<td>0.3</td>
<td>10</td>
<td>1750</td>
<td>30</td>
<td>2.6</td>
<td>520</td>
<td>1.5</td>
<td>32,227</td>
<td>1.74</td>
<td>n.d.</td>
</tr>
<tr>
<td>5</td>
<td>(1)</td>
<td>A</td>
<td>0.6</td>
<td>21</td>
<td>1600</td>
<td>30</td>
<td>1.5</td>
<td>124</td>
<td>1.7</td>
<td>19,705</td>
<td>n.d.</td>
<td>131.5</td>
</tr>
<tr>
<td>6</td>
<td>(1)</td>
<td>A</td>
<td>0.9</td>
<td>25</td>
<td>1400</td>
<td>50</td>
<td>2.6</td>
<td>58</td>
<td>5.9</td>
<td>17324</td>
<td>2.49</td>
<td>132.0</td>
</tr>
<tr>
<td>7</td>
<td>(1)</td>
<td>A</td>
<td>1.2</td>
<td>19</td>
<td>1750</td>
<td>55</td>
<td>1.3</td>
<td>74</td>
<td>22</td>
<td>13952</td>
<td>2.65</td>
<td>130.8</td>
</tr>
<tr>
<td>8</td>
<td>(1)</td>
<td>A</td>
<td>1.2</td>
<td>10</td>
<td>1750</td>
<td>60</td>
<td>0.4</td>
<td>40</td>
<td>26</td>
<td>15317</td>
<td>2.62</td>
<td>n.d.</td>
</tr>
<tr>
<td>9</td>
<td>(1)</td>
<td>A</td>
<td>1.5</td>
<td>17</td>
<td>1950</td>
<td>50</td>
<td>1.2</td>
<td>84</td>
<td>52</td>
<td>10438</td>
<td>4.44</td>
<td>126.5</td>
</tr>
<tr>
<td>10</td>
<td>(1)</td>
<td>B</td>
<td>0.3</td>
<td>20</td>
<td>860</td>
<td>30</td>
<td>1.3</td>
<td>890</td>
<td>0.2</td>
<td>12,307</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>11</td>
<td>(1)</td>
<td>B</td>
<td>0.3</td>
<td>20</td>
<td>1650</td>
<td>45</td>
<td>0.4</td>
<td>222</td>
<td>0.2</td>
<td>33,090</td>
<td>n.d.</td>
<td>136.0</td>
</tr>
<tr>
<td>12</td>
<td>(1)</td>
<td>B</td>
<td>0.3</td>
<td>19</td>
<td>875</td>
<td>45</td>
<td>1.2</td>
<td>170</td>
<td>0.4</td>
<td>39400</td>
<td>1.87</td>
<td>135.8</td>
</tr>
<tr>
<td>13</td>
<td>(1)</td>
<td>B</td>
<td>0.7</td>
<td>38</td>
<td>875</td>
<td>45</td>
<td>8.9</td>
<td>13</td>
<td>0.9</td>
<td>15800</td>
<td>1.98</td>
<td>130.2</td>
</tr>
<tr>
<td>14</td>
<td>(1)</td>
<td>B</td>
<td>2.1</td>
<td>38</td>
<td>875</td>
<td>60</td>
<td>3.3</td>
<td>16</td>
<td>28</td>
<td>21,648</td>
<td>n.d.</td>
<td>127.1</td>
</tr>
<tr>
<td>15</td>
<td>(2)</td>
<td>n.a.</td>
<td>0.3</td>
<td>1000</td>
<td>0.5</td>
<td>60</td>
<td>2.4</td>
<td>4</td>
<td>100</td>
<td>2894</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>16</td>
<td>(3)</td>
<td>n.a.</td>
<td>0.3</td>
<td>55</td>
<td>n.a.</td>
<td>90</td>
<td>0.37</td>
<td>0</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Polym. Temp was 20 °C, except for runs 4, 8, 13 and 14 at 60 °C; Ethylene: 2 bar at 20 °C and 4 bar at 60 °C, ([ethylene] ≈ 0.29 M); solvent: toluene, total solution volume: 250 ml; Method A: premixed catalyst before adding MA after 15 min (0 min for HDPE); Method B: mixed catalyst after addition of MA; a: activity in kg polymer / (mol Cat × h); b: all molecular weight data in this table based on calibration with PS-standards; c: HDPE run; d: ethylene flow problem (last 3 min of run); n.d.: not determined, n.a.: not applicable.
All copolymerization runs were carried out for less or equal to 60 min. The acrylate conversion stayed below 5% thereby avoiding a compositional drift in the batch polymerizations. We observed a decrease in the activities as the concentration of methyl acrylate increased. When comparing the 2 methods of addition, they are higher when the catalyst components are premixed as in Method A, then when they are introduced in Method B and the resulting polymer microstructure is also not different between the two methods. Even in the presence of ethylene, the chiral metallocene only forms PMA. Claverie and Spitz had found that the nickel enolate catalyst would copolymerize an ester with a long spacer group in ethyl 10-undecanoate but it does not polymerize acrylate. For comparison purpose we used AIBN to make true copolymer.

![Figure 12: Polymerization rate based on ethylene consumption versus polymerization time.](image)
Figure 12 shows the polymerization rate based on the ethylene consumption versus polymerization time at $T_p = 20\, ^\circ C$ ($\pm 1.5\, ^\circ C$), except for experiment # 8 at $60\, ^\circ C$ ($\pm 3\, ^\circ C$). The sharp drop within the first 100 s is caused by the completion of the saturation of the solvent with ethylene. In case of polyethylene run (Expt # 1) the catalyst solution was injected after the saturation with ethylene had been completed.

From the Table 3, looking at experiment # 1 for HDPE and experiments # 8 and 9 for Method B addition (i.e. when the catalyst is added after monomers are introduced), it still needs to form active centers and the activity goes through a slight maximum before it decreases.

Using a mass flow meter, we measured the ethylene uptake in to the reactor and we observed a decrease in the polymerization rate over time, which is one of the characteristics of the iron-based catalyst. Also as the concentration of the methyl acrylate increased, the activity dropped. In contrast, for the same time periods (i.e. 30 min to 1 h) the polymerization activity of a similar metallocene/MAO catalyst in ethylene/1-olefin polymerization stays constant.

Because of reactions of the acrylate with the MAO, Method B leads generally to lower activities than Method A. In all the copolymerizations the decrease in activity is not as rapid as in the case of polyethylene. Also for the higher concentrations of acrylate, the decrease of the rate with time is less steep. For further higher concentrations of acrylate the polymerization rate reaches a minimum level eventually leading to the overlapping of the kinetic curves.
From the data in Table 3 it is not possible to determine the copolymerization reactivity ratios over the entire range because of the low correlation and fit with the binary copolymerization model. DSC measurements provide another evidence that true copolymers are not formed. Only one peak for polyethylene can be detected in the DSC diagrams, since the polymethyl acrylate is totally amorphous.

Once more than 20 mol % of the acrylate have been polymerized the melting temperature of the polymers does not decrease below 125 °C as one would expect for true copolymers. In fact a commercial copolymer, Optema TC 120® (from ExxonMobil) containing ca. 8 mol % MA has a melting point of 73 °C. No significant amount of methyl acrylate is copolymerized with ethylene. It is possible that the molecular weight causes some of the decrease in the melting points as the methyl acrylate concentration increases. The PMA dissolves under the mixing in chloroform much better than the remainder of the polymer. Also the formed polymer is not rubbery, thus excluding the possibility of block copolymerizations.
Figure 13: Typical IR spectrum of a copolymer

Figure 13 shows the typical IR spectrum of an Ethylene-Methyl acrylate “copolymer”. The pronounced carbonyl band at ca. 1740 cm$^{-1}$ indicates that acrylate is present in the produced polymer.

In order to clarify if the products are true copolymers or not, we applied H NMR spectroscopy as an efficient method. Figure 14 shows the peak assignments for the H NMR spectra of the polymers. Figure 15 shows the H NMR spectra of a “copolymer” made with iron based catalyst 1 (Exp. 9) in comparison to a blend containing 35mol % MA and a true copolymer made by radical copolymerizations initiated by AIBN. In all the copolymers made with catalyst 1 the maximum peak in the aliphatic region occurs at
1.28 ppm. However the true ethylene methylacrylate copolymers with 52 % acrylate produce the largest peak at 1.45 ppm and a characteristic peak at 1.55 ppm. The peak at 1.28 ppm is assigned to the uniform methylene protons of HDPE. The peak at 1.45 ppm is caused by the protons of one of the methylene groups of an ethylene unit, which are adjacent to the methylene group of an acrylate unit. The peak at 1.55 ppm is assigned to the methylene protons of a methyl acrylate unit being next to an ethylene unit. \(^{36,37}\)

The three symmetrically distributed multiplets between 2.1 and 1.4 ppm are usually observed for a pseudo copolymer, which are characteristic for PMA. However in the case of an actual copolymer the multiplet structure has been replaced by a slanted sequence of peaks close to the peak at 1.45 ppm.

![Chemical structures](image)

**Figure 14:** Peak assignments in H NMR spectra

Also based on H NMR spectroscopy for the copolymers containing higher than 20 % MA about 0.5 to maximum 5 methyl end groups per 1000 C-atoms can be estimated
from the peak around 0.90 ppm without presence of any unsaturated end groups. Also, IR-spectroscopy confirmed that unsaturated end groups were hardly present.

**Figure 15:** $^1$H NMR spectra measured in C$_2$D$_2$Cl$_4$ at 120 °C; top: true E/MA copolymer made with AIBN containing 68 % MA; middle: polymer formed with catalyst (I) using Method of Addition A, containing 52 % MA, (Experiment # 9); bottom: a mixed blend of polyethylene and PMA containing 35 % MA. The peaks marked “x” in the spectrum at
the top are from the initiator residue tetramethylsuccinonitrile; “s” stands for solvent residue (toluene).

We also conducted C 13 NMR spectroscopy on our polymers. The peak assignments are given in Figure 16.

**Figure 16:** Peak assignments for C 13 NMR spectra.
Figure 17: C-13 NMR spectra measured in C$_2$D$_2$Cl$_4$ at 120 °C; top: true E/MA copolymer made with AIBN containing 68 % MA; middle: polymer formed with catalyst (I) using Method of Addition A, containing 52 % MA, (Experiment # 9); bottom: a mixed blend of polyethylene and PMA containing 35 % MA. The peaks marked “x” in the spectrum at the top are from the initiator residue tetramethylsuccinonitrile.
The C 13 NMR spectra support again the fact that the copolymers obtained with catalyst 1 are blends of the two homopolymers rather than copolymers.

**Figure 18:** Typical TGA spectrum for the copolymer.

Figure 18, shows the TGA spectrum for the Ethylene - Methyl acrylate copolymer. The above TGA spectrum is for the polymer sample that is washed with 50 ml of HCL and methanol at the end of the run. HCL is used to clean the polymer from any residue of the catalyst.
Figure 19: Typical DSC spectrum for a copolymer

Figure 19 shows the DSC spectrum for Ethylene – Methyl acrylate copolymer. Due to the presence of a high and a low molecular weight tail of polymer and also because of the increased chain transfer with the relatively high amount of MAO, we observed a broad molecular weight distribution for the polyethylene (Mw = 83245 g/mol, Mn = 3832, PDI = 2.17), as had been reported earlier. However, the molecular weight and the PDI decrease when methyl acrylate is introduced into the system.

In Table 4 the glass transition temperatures of the HDPE and PMA, our polymers and the true copolymers are shown. In the case of our polymers two distinct Tg-values corresponding to those of the two homopolymers can be observed. However, only in the
true copolymer a single glass transition occurs between the values for the homopolymers. This again confirms that only blends of polyethylene and PMA are formed in our case.

**Table 4 – Selected glass transition temperatures of homopolymers, “copolymer”-blends produced with (I), and a true copolymer made with AIBN from DSC measurements**

<table>
<thead>
<tr>
<th>Entry</th>
<th>T_{g1}</th>
<th>Cp1</th>
<th>T_{g2}</th>
<th>Cp2</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1(HDPE)</td>
<td>-111.7</td>
<td>0.018</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>6</td>
<td>-119.6</td>
<td>0.011</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>-112.8</td>
<td>0.025</td>
<td>3.9</td>
<td>0.069</td>
</tr>
<tr>
<td>9</td>
<td>-117.1</td>
<td>0.008</td>
<td>10.9</td>
<td>0.175</td>
</tr>
<tr>
<td>13</td>
<td>-114</td>
<td>0.010</td>
<td>9.2</td>
<td>0.045</td>
</tr>
<tr>
<td>27(PMA)</td>
<td>12.3</td>
<td>0.414</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>E/MA Cop^a</td>
<td>-18.8</td>
<td>0.756</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

^a: true copolymer made with AIBN containing 68 % methyl acrylate, this amorphous copolymer showed no major endothermic peak; n.d.: not detectable; n.a.: not applicable.

The distribution becomes significantly narrower (M_w/M_n = 2.40) as compared to the regular polyethylene obtained with catalyst 1 (Experiment # 1). This is because there is a loss of both high and low molecular weight fractions. As the chain transfer to the acrylate takes place, the high molecular weight portion of the polyethylene decreases. The chain transfer with the aluminum causes the low molecular weight tail. The low molecular weight tail may decrease because some of the MAO is consumed by the reaction with the acrylate, and cannot cause additional chain transfer to form lower
molecular weight polyethylene. As further methyl acrylate is added the PDI increases again due to formation of an increasingly larger, low molecular weight fraction of PMA.
Part II: HOMPOLYMERIZATION OF METHYL ACRYLATE

In the case of Methyl acrylate homopolymerizations, comparing the activities of all 3 catalyst systems (iron based catalyst 1, zirconium catalyst 2 and nickel based catalyst 3) for the polymerization of methyl acrylate (MA)

**TABLE 5: Conditions and activities for the polymerization of methyl acrylate with three single-site catalysts**

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Catalyst Type</th>
<th>Catalyst Mmol</th>
<th>Cocatalyst /Catalyst -Ratio</th>
<th>t min</th>
<th>T °C</th>
<th>Yield g</th>
<th>Activity$^a$</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>(1)</td>
<td>7</td>
<td>950</td>
<td>15</td>
<td>60</td>
<td>2.0</td>
<td>1133</td>
<td>133000</td>
<td>2.38</td>
</tr>
<tr>
<td>18</td>
<td>(1)</td>
<td>7</td>
<td>950</td>
<td>30</td>
<td>60</td>
<td>2.1</td>
<td>595</td>
<td>64,700</td>
<td>1.98</td>
</tr>
<tr>
<td>19</td>
<td>(1)</td>
<td>8</td>
<td>800</td>
<td>45</td>
<td>60</td>
<td>2.3</td>
<td>381</td>
<td>125,000</td>
<td>2.25</td>
</tr>
<tr>
<td>20</td>
<td>(1)</td>
<td>7</td>
<td>900</td>
<td>60</td>
<td>60</td>
<td>1.5</td>
<td>215</td>
<td>122,000</td>
<td>2.24</td>
</tr>
<tr>
<td>21</td>
<td>(1)</td>
<td>7</td>
<td>950</td>
<td>120</td>
<td>60</td>
<td>4.0</td>
<td>283</td>
<td>140,000</td>
<td>2.46</td>
</tr>
<tr>
<td>22</td>
<td>(1)</td>
<td>9</td>
<td>100</td>
<td>60</td>
<td>60</td>
<td>0.61</td>
<td>68</td>
<td>279,000</td>
<td>2.44</td>
</tr>
<tr>
<td>23</td>
<td>(1)</td>
<td>8</td>
<td>200</td>
<td>60</td>
<td>60</td>
<td>0.68</td>
<td>85</td>
<td>164,000</td>
<td>1.65</td>
</tr>
<tr>
<td>24</td>
<td>(1)</td>
<td>8</td>
<td>425</td>
<td>60</td>
<td>60</td>
<td>2.0</td>
<td>256</td>
<td>179,000</td>
<td>2.25</td>
</tr>
<tr>
<td>25</td>
<td>(1)</td>
<td>7</td>
<td>1850</td>
<td>60</td>
<td>60</td>
<td>0.92</td>
<td>132</td>
<td>56,500</td>
<td>1.92</td>
</tr>
<tr>
<td>26</td>
<td>(1)</td>
<td>8</td>
<td>800</td>
<td>60</td>
<td>80</td>
<td>1.2</td>
<td>155</td>
<td>96,100</td>
<td>1.96</td>
</tr>
<tr>
<td>27</td>
<td>(1)</td>
<td>8</td>
<td>850</td>
<td>60</td>
<td>40</td>
<td>0.53</td>
<td>66</td>
<td>115,000</td>
<td>1.79</td>
</tr>
<tr>
<td>28</td>
<td>(1)</td>
<td>8</td>
<td>830</td>
<td>60</td>
<td>20</td>
<td>0.30</td>
<td>37</td>
<td>138,000</td>
<td>1.74</td>
</tr>
<tr>
<td>29</td>
<td>(1)</td>
<td>7</td>
<td>900</td>
<td>60</td>
<td>0</td>
<td>0.02</td>
<td>3</td>
<td>152,000</td>
<td>2.28</td>
</tr>
<tr>
<td>30</td>
<td>(1)</td>
<td>8</td>
<td>830</td>
<td>60</td>
<td>60</td>
<td>0.30</td>
<td>185</td>
<td>83,000</td>
<td>1.62</td>
</tr>
<tr>
<td>31</td>
<td>(2)</td>
<td>200</td>
<td>0.5</td>
<td>15</td>
<td>60</td>
<td>1.9</td>
<td>38</td>
<td>36,000</td>
<td>3.23</td>
</tr>
<tr>
<td>32</td>
<td>(2)</td>
<td>190</td>
<td>0.5</td>
<td>30</td>
<td>60</td>
<td>5.9</td>
<td>62</td>
<td>138,000</td>
<td>2.46</td>
</tr>
<tr>
<td>33</td>
<td>(2)</td>
<td>200</td>
<td>0.5</td>
<td>45</td>
<td>60</td>
<td>8.4</td>
<td>56</td>
<td>168,000</td>
<td>2.72</td>
</tr>
<tr>
<td>34</td>
<td>(2)</td>
<td>200</td>
<td>0.5</td>
<td>60</td>
<td>60</td>
<td>4.8</td>
<td>24</td>
<td>157,000</td>
<td>2.35</td>
</tr>
<tr>
<td>35</td>
<td>(2)</td>
<td>190</td>
<td>0.5</td>
<td>120</td>
<td>60</td>
<td>8.4</td>
<td>22</td>
<td>281,000</td>
<td>3.97</td>
</tr>
<tr>
<td>36</td>
<td>(3)</td>
<td>14</td>
<td>n.a.</td>
<td>15</td>
<td>60</td>
<td>0</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>37</td>
<td>(3)</td>
<td>1295</td>
<td>n.a.</td>
<td>120</td>
<td>60</td>
<td>0.1</td>
<td>&gt; 0.05</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

*Methyl acrylate: 5.55 M; Solution volume: 50 ml(except for experiment 16 with 400 ml); Solvent: Toluene, all molecular weight data in this table based on calibration with PMMA standards; a: activity in [kg PMA / (mol of cat x h)]; b: run with 16.9 mg of galvinoxyl; n.a.: not applicable; n.d.: not determined*
From the Table 5, looking at the activities column, it is very clear that the overall activities of the iron based catalyst 1 are higher in magnitude than those of the chiral zirconocene catalyst 2. In order to have reproducible polymerization rates, the metallocene catalyst was kept close to a concentration of 200 µmol. We also experimented according to literature procedure\textsuperscript{21} by adding diethyl zinc. However, this method leads actually to less reliable polymerization activities. Nickel enolate catalyst 3 is only active above 55 °C, so even the other catalyst runs were carried out at 60 °C to be better able to compare them with the two other catalysts\textsuperscript{20}. The nickel enolate catalyst 3 did not work in polymerizing methyl acrylate.

![Kinetic plot for polymerization of methyl acrylate with catalysts 1 and 2](image)

**Figure 20**: Kinetic plot for polymerization of methyl acrylate with catalysts 1 and 2

Figure 20 shows the polymerization kinetics comparison for the polymethyl acrylate (PMA) runs with catalysts 1 and 2. The kinetic data is obtained by running a series of polymerizations at different lengths of times.
From the Figure 20 it is evident that the activity of the PMA runs with catalyst 1 within the first few minutes of the polymerization reaches a maximum and then decreases rapidly. Also for the polymerizations with ethylene, with the same catalyst system, a similar pattern had been observed.

**Figure 21:** Dependence of Polymerization activity on Al/Fe-ratio

Figure 21 shows the dependence of the polymerization activity on the ratio of methyl aluminoxane to the iron based catalyst system 1. It was observed that the polymerization activity reaches a maximum at a molar ratio of ca. 500:1. Active polymerization centers are possible only at high MAO ratios. The optimum for this cocatalyst / catalyst ratio can be explained because of the nature of the MAO, which is an oligomeric and non uniform compound. Only a small portion of the used MAO forms active polymerization centers. If the MAO concentration is higher than the optimum then deactivation of the active species occur. This is mainly because of the side reactions with the aluminum organyls.
For the second catalyst system, i.e. for the metallocene/borane catalysts, in order to obtain high polymerization activities, the B/Zr ratio must be in the range of 1:1 and 1:2. The latter ratio appears to be preferable with acrylates.

In Figure 22, the influence of polymerization temperature on the activity is shown. It is evident from the graph that the activity increases from 0 to 60 °C, but later, above 60 °C the activity starts to diminish. One of the characteristics of these polymerizations is that the activity should increase with the rise in temperature. However, the destabilization of the methyl aluminoxane at the relatively high temperature and the one-hour long run seems to be the main reason for the loss in activity close to 80 °C.

![Figure 22: Influence of polymerization temperature on activity](image-url)
Molecular weight properties

![Influence of polymerization temperature on molecular weight](image)

Figure 23: Influence of polymerization temperature on molecular weight

In Figure 23 the effect of temperature on the molecular weight ($M_n$) is shown. One of the typical tendencies in chain polymerization is that the molecular weight drops as the polymerization temperature increases. This effect is evident from the figure above. From the data in the Table 5 it can be seen from experiment # 17 and 19 that the molecular weight increases with time. There was no much change in the polydispersity for the given temperature range. The molecular weights that were obtained were reasonably high. This indicated that there was a moderate chain transfer with the late transition metal catalyst 1. From Table 5, comparing experiments 19 and 33, the molecular weight with catalyst 1 is slightly lower than with the chiral metallocene catalyst 2. The relatively narrow polydispersities ($M_w/M_n$) close to 2 are typical for single site catalysts.
Increasing the cocatalyst/catalyst ratio leads to a marked decrease of the molecular weight relatively, as shown in Figure 24. One of the main reasons for this effect is due to the dominant chain transfer reactions to the methyl aluminoxane. The same effect had also been observed for the homopolymerizations of ethylene\textsuperscript{41}. However as shown in the Figure 25, the polydispersities tends to decrease as the Al/Fe- ratio increases. The latter effect is different from the relationship in the case of polyethylene. It had been reported that for polyethylene the polydispersity increased with increasing Al/Fe ratio\textsuperscript{19}.

![Dependence of the number average molecular weight on Al/Fe-ratio](image)

*Figure 24: Influence of the number average molecular weight on Al/Fe-ratio*
Figure 25: Influence of the polydispersity index on Al/Fe-ratio

NMR spectra and Tacticity of the Polymethyl Acrylate.

Figure 26: $^1H$ NMR of a polymethyl acrylate measured in CDCl3
Figure 26 shows H NMR spectrum of a poly methyl acrylate made with the iron based catalyst 1 and measured in CDCl3. Previous studies have already been done on the peak assignments of the H NMR spectra of the PMA\textsuperscript{36-39}. In chloroform as solvent the three multipletts at 1.93, 1.68, 1.55 ppm are caused by methylene protons. The methine proton appears at 2.3 ppm and methoxy protons appears at 3.6 ppm. In the expansion given in Figure 25 the small triplet at ca. 0.88 ppm originates from methyl protons representing end groups. No peak in the area between 4.5 to 7 ppm are observed, which excludes the presence of unsaturated end groups for these polymers.

The three peaks, shown in Figure 27, can be separated better in deuterated 1,1,2,2-tetrachloroethane at high temperatures than in chloroform, though the latter is usually sufficient for quantitative evaluations. A typical sequence for isotactic PMA is explained in the Figure 19. The peaks at 1.55 and 1.93 ppm are caused by the non equivalent protons Ha and Ha’’ respectively, which represent a meso diad. The peak at 1.68 ppm is caused by equivalent protons Ha, which corresponds to a racemo diad. This is a sequence typical in syndiotactic PMA.
Figure 27: Top: Differentiation between protons associated with meso and racemo diads. Middle and bottom: Expanded regions from H NMR’s in CDCl3 for polymethyl acrylate made with the iron based catalyst (1), and polymethyl acrylate made with the chiral metallocene (2), respectively.
A comparison has been made between a PMA made with iron based catalyst 1 with that of the chiral metallocene 2. In the middle and bottom portions of Figure 27 the expanded, critical regions from 1.35 pm to 2.15 ppm are shown. The percentages of racemo and meso sequences are calculated from the peak integrals and are given in Table 5. Since the m and r sequences are close to equal ratios, we can predict that the PMA’s produced with the Fe based catalyst are atactic. For the metallocene catalyst, the tacticity in this case is still below 90%. The mechanism by which the methyl acrylate polymerizes with catalyst 1 is also different from that of propylene. Brookhart had shown that the applied catalyst 1 forms isotactic polypropylene involving 2-1 additions. However, this had occurred only at low polymerization temperatures of 20 °C.

Table 6. Percentages of racemo and meso diads in dependence of main polymerization parameters.

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>[Cocatalyst]/[Catalyst]</th>
<th>T</th>
<th>% r</th>
<th>% m</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>(1)</td>
<td>950</td>
<td>60</td>
<td>53.23</td>
<td>46.77</td>
</tr>
<tr>
<td>18</td>
<td>(1)</td>
<td>900</td>
<td>60</td>
<td>51.47</td>
<td>48.53</td>
</tr>
<tr>
<td>20</td>
<td>(1)</td>
<td>100</td>
<td>60</td>
<td>53.62</td>
<td>46.49</td>
</tr>
<tr>
<td>21</td>
<td>(1)</td>
<td>200</td>
<td>60</td>
<td>51.58</td>
<td>48.42</td>
</tr>
<tr>
<td>22</td>
<td>(1)</td>
<td>425</td>
<td>60</td>
<td>52.91</td>
<td>47.10</td>
</tr>
<tr>
<td>23</td>
<td>(1)</td>
<td>1850</td>
<td>60</td>
<td>50.50</td>
<td>49.50</td>
</tr>
<tr>
<td>24</td>
<td>(1)</td>
<td>800</td>
<td>80</td>
<td>52.74</td>
<td>47.26</td>
</tr>
<tr>
<td>25</td>
<td>(1)</td>
<td>850</td>
<td>40</td>
<td>50.39</td>
<td>49.61</td>
</tr>
<tr>
<td>26</td>
<td>(1)</td>
<td>830</td>
<td>20</td>
<td>49.57</td>
<td>50.43</td>
</tr>
<tr>
<td>27</td>
<td>(1)</td>
<td>900</td>
<td>0</td>
<td>48.30</td>
<td>51.70</td>
</tr>
<tr>
<td>33</td>
<td>(2)</td>
<td>0.5</td>
<td>60</td>
<td>29.94</td>
<td>70.06</td>
</tr>
</tbody>
</table>
Figure 28: Influence of the Al/Fe-ratio on tacticity of polymethyl acrylate with catalyst 1

Figure 29: Influence of the degree of tacticity of polymethyl acrylate on temperature.
In the Figure 28, the influence of the Al/Fe ratio over the degree of tacticity is shown. Figure 29 shows the influence of the degree of tacticity on temperature. It is observed that the degree of tacticity increases as the temperature is lowered. The molecular weight and the activity decreases at the same time. Also with the increasing concentration of MAO, the percentage of meso diads also increases. Other researchers have indicated that there are some reactions occurring between the MAO and the acrylate\textsuperscript{40}. The influence on the MAO on the polymerization mechanism is quite complex as already observed for the polymerization of ethylene.
CHAPTER IV

DISCUSSION
**DISCUSSION**

In this work, sufficient evidence is provided to show that the polymerization of methyl acrylate with iron based catalyst is not initiated by a radical species but follows primarily via a coordinative mechanism as expected for single site catalysts. Previously it has been reported that the addition of inhibitors do not prevent coordinatively initiated polymerization\textsuperscript{24}. But at low catalyst concentrations, even though the inhibitor is not removed, the polymerization still occurs. Also the removal of inhibitor does not increase the polymerization activity. From table 5, experiment # 30, it is evident that the addition of galvinoxyl did not lead to a decrease in polymer formation. It has been argued that a test with galvinoxyl would not be necessary conclusive regarding the type of polymerization initiator, particularly if the influence is negative\textsuperscript{22,23}.

The following points further prove that the polymerizations follow a coordinative mechanism. One of the main evidence that supports coordinative mechanism is that as the temperature decreases and the Al/Fe ratio increases, the tacticity of the polymer also increases. In addition, the maximum polymerization activity at a certain Al/Fe ratio can be explained if a coordination system has been formed. Finally, with the present catalyst ethylene polymerizes at a much faster rate than methyl acrylate. This is not true in free radical polymerization. In free radical polymerization the rates of the homopolymerizations of the two monomers are reversed, i.e. the acrylate would have polymerized faster than ethylene.
During the copolymerization runs, it has been shown that there was no cross-polymerization occurring. The formed polymer was a blend of two homopolymers. This means that there were at least two different active polymerization centers formed in the copolymerizations. Also the PMA does not contain any unsaturated end groups. It has also been shown that the effect of temperature and Al/Fe ratio is different in the homopolymerization of ethylene and PMA. In the polymerization of methyl acrylate a coordinative bond is formed between the metal and carbonyl oxygen. This is true in the cases of other single site catalysts as well\textsuperscript{25-30}. Whereas the ethylene polymerization proceeds via a metal-pi-bond coordination. This is in contrast to the case of methyl acrylate, as in this case, with some palladium catalysts; a pi-bond complexation with the double bond of the acrylate is favored\textsuperscript{31}. However, the reason these Pd-catalyst can copolymerize both ethylene and the acrylate is because of a simultaneous chain walking mechanism which leads to the acrylate forming endgroups\textsuperscript{25,32}.

Scheme 10 shows the pathways along which the two monomers, MA and ethylene, undergo polymerization. In the case of iron-based catalyst, the ethylene polymerization involves formation of at least two active species, which are cationic and neutral\textsuperscript{33-35}. Hence for the iron-based copolymerizations, these additional active centers keep forming polyethylene even while polymerizing the acrylate. The polymerization of the methyl acrylate resembles a GTP-like insertion and involves a cationic enolate complex. It has been mentioned that the insertion of ethylene following the formation of the enolate is thermodynamically not favored (endothermic). In the case of the metallocene catalyst, because one predominant, cationic species is formed, which only can polymerize the acrylate, only PMA, but no polyethylene is produced. Further
investigations are required to fully elucidate the mechanism in particular for the polymerization of ethylene with catalyst 1.

**Scheme 10**: Proposed pathways for the simultaneous polymerization of methyl acrylate and ethylene by the iron based catalyst (1)
CHAPTER V

CONCLUSIONS
CONCLUSIONS

Comparing catalyst 1 (iron based) and catalyst 2 (metallocene), polymethyl acrylate can be produced at high activities with the applied iron based catalyst than those of a metallocene catalyst system. The polymerization mechanism follows a coordinative mechanism. The obtained polymers are atactic, but can be still used for many relevant applications such as adhesives or compatibilizers. The polydispersities of the obtained polymers are close to 2, as is typical for single site catalysts. The obtained molecular weights are also sufficiently high. An Al/Fe ratio and temperature range to obtain maximum polymerization activities could be identified. In polymerizations with ethylene, high formation of polymethylacrylate exceeding that of polyethylene was possible at activities surpassing those of the homopolymerization of the methyl acrylate. Using H-NMR spectroscopy and DSC measurements, it could be demonstrated that polymer blends are formed and not true copolymers.
CHAPTER VI

REFERENCES
REFERENCES:


2) Chemical Engineer C & EN., June 25, 2001


14) www.exxon.mobil.com


42) Mai, X., M.S. Thesis (Chemistry), Rochester Institute of Technology
43) Florian M. B.; Mubarik M. Chowdhry; Stefan Mecking, Macromolecules, 2003, 36, 6711-6715